PREPARATION AND CHARACTERISATION OF POLYMER COMPOSITES WITH BLOODMEAL

by

CHERYL-ANN ELIZABETH CLARKE (B.Sc. Hons.)

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Department of Chemistry

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Declaration

I hereby declare that the research in this thesis is my own independent work, and has not previously been submitted to any other University in order to obtain a degree. I further cede copyright of the dissertation in favour of the University of the Free State.

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Ms. C.E. Clarke

Dedication

This work is dedicated to my parents, my mother Maryncha Clarke, and my late father, Robert Clarke. Thank you for your eternal and unwavering reassurance and support, through everything that life has thrown at us. I would also like to thank my brothers, Christopher and Richard Clarke for always being there for me. Lastly, I don't think I would have come this far without the motivation and determination inspired by my amazing husband, Quintin König. I love you, you are my rock! Thank you for everything!

Abstract

This research focuses on the fabrication of composites produced by the combination of BM (bloodmeal) with HDPE (high-density polyethylene). HDPE was chosen because it is amongst the most widely used synthetic plastic material worldwide, thus a study of improving the degradability of these materials can be regarded as worthwhile. HDPE was combined with dried BM. The BM was blended with the polymers using mechanical mixing at 150 °C and subsequent melt-pressing at the same temperature into films of different thicknesses. The morphology, thermal and mechanical properties, and water absorption were investigated using moisture analysis, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), optical microscopy, scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy, and tensile testing before and after periods of underground ageing. Moisture analysis revealed that the addition of BM to HDPE moderately increased the moisture content of the composites. Morphological investigations showed good dispersion of BM in the polyethylene matrix, but the effects of ageing were not highly evident. DSC results indicated that the presence of BM did not significantly influence the crystallization behaviour of HDPE since the melting temperatures and melting enthalpies varied only slightly for each composition. The mechanical properties for BM composites for all ageing times showed similar trends, such as a large initial increase in modulus for 1% BM added. The modulus decreased slightly as the BM content increased. Overall, the mechanical properties remained relatively constant with underground ageing time. In conclusion, it seems as if the presence of BM in HDPE had an influence on the mechanical properties and water absorption behaviour of the composites, but did not observably accelerate the underground environmental degradation of this polymer over periods as long as 36 weeks.

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List of symbols and abbreviations

ATR-FTIR	attenuated total reflectance Fourier-transform infrared spectroscopy
BM	bloodmeal
E_4	average modulus after four weeks of underground ageing (first ageing time)
E_{36}	average modulus after thirty six weeks of underground ageing (final ageing time)
ΔH_c	enthalpy of crystallization
ΔH_c^{norm}	normalised enthalpy of crystallization
ΔH_m	enthalpy of melting
ΔH_m^{norm}	normalised enthalpy of melting
DNA	deoxyribonucleic acid
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
ESC	environmental stress cracking
FTIR	Fourier-transform infrared spectroscopy
GPC	gel permeation chromatography
IR	infrared
HDPE	High-density polyethylene
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
$M_{initial}$	initial mass
MS	mass spectrometry
M_{wet}	mass after immersion
NMR	nuclear magnetic resonance
PE	Polyethylene
PLA	poly(lactic acid)
POM	polarized optical microscopy
SDS	sodium dodecyl sulphate
SEM	scanning electron microscopy
TGA	thermogravimetric analysis
T_c	crystallization temperature

T_g	glass transition temperature
T_m	melting temperature
UHMWPE	ultra-high molecular weight polyethylene
ULMWPE	ultra-low molecular weight polyethylene
UV	ultra violet
XRD	X-ray diffraction

Chapter 1

Introduction

1.1. Overview

Polymers are applied in a broad variety of products and are utilised in an extensive range of industries. Synthetic polymers are derived from non-renewable raw materials, and as these oil reserves are consumed, the cost of this resource escalates. These man-made materials are persistent in the environment, so numerous studies of substitutes for synthetic polymer materials have taken place. In addition, a significant amount of research has been applied to the study of degradable polymers to alleviate the adverse impact on the environment [1-3]. This chapter consists of an introduction to, and a literature review of protein/polymer composites, and in particular, bloodmeal and bloodmeal/polymer composite classifications and properties.

1.2. Polyethylene: Classification and properties

Polyethylene (PE) is currently one of the most widely used synthetic materials due to its low cost, simple processing, good mechanical properties, superior chemical resistance and light weight. Polyethylene has a very simple structure, and is one of the simplest commercial polymers. The polymer consists of ethylene monomers polymerised under specific temperature and pressure conditions through the action of catalysts, resulting in a long chain of carbon atoms with two hydrogen atoms attached to each carbon atom. Polymerisation conditions influence the incidence of secondary chains that branch out from the primary chain. Polyethylene can be arranged into sub-groups such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), ultra-high-molecular-weight polyethylene (UHMWPE), and ultra-low-molecular-weight polyethylene (ULMWPE), to name a few. The difference between the polyethylene sub-groups is based on variables such as the extent and type of branching, the crystal structure and the molecular weight, which also directly affects the characteristics of the material [4].

LDPE is produced under high pressure conditions and the end product is a polymer with a large degree of branching, consequently the long polymer chains cannot pack tightly together and thus LDPE possesses a lower density than HDPE. The manufacture of HDPE occurs at lower pressures and the polymer consists of very long, straight chains with a low degree of branching. HDPE has higher crystallinity than LDPE since the HDPE polymer chains are more linear than the LDPE chains, which results in more effective packing into crystal lamellae. Consequently, the properties of HDPE and LDPE will vary slightly [4].

Polyethylene can be utilised in its pure form, or in blends with other natural or synthetic polymers, resulting in a large range of materials. Various fillers can also be incorporated in the processing of polyethylene to augment or integrate useful properties in the end product. Applications are highly varied and include products in almost every industry, from the food packaging industry, agriculture, children's toys, shopping bags and even in the medical industry [5,6].

Polyethylene is resilient to degradation given that it is made up of long hydrophobic carbon chains and possesses high molecular weight that makes it resistant to hydrolysis and microbial attack. The PE products will not biodegrade unless it is subjected to specified treatment or if biodegradable fillers are included during plastic processing. The fact that it does not biodegrade results in vast accumulation of wastes that can have devastating effects on the ecosystem of an area [5]. Increasing the biodegradable character of polyethylene, without significantly altering the fundamental properties and adversely affecting the functionality, would prove to be useful taking into consideration the fact that polyethylene is so extensively utilised.

1.3. Literature review

1.3.1. Polymers and (bio)degradability

A synthetic polymer is a "man-made" material, derived from petroleum oil and is designed by scientists and engineers to serve a specific purpose. Properties of synthetic polymers vary greatly. Thermosetting polymers are materials that soften when heated but become permanently hard and rigid after cooling as a result of the formation of covalent bonds between molecules. Epoxy resins or rubber that has been vulcanised, are examples of thermosetting polymers.

Thermoplastics, such as polyethylene, are materials that become soft and flexible on heating and subsequently solidify and harden upon cooling. The softening and hardening process can be repeated as required, thus thermoplastic polymers are fairly easy to process [4].

Physical properties of polymers, such as melting temperature (T_m) and glass transition temperature (T_g), also vary, and these properties are directly related to features such as the degree of crystallinity, extent of chain branching or the amount of cross-linking. These features can help to differentiate a material into sub-groups such as high-density polyethylene (HDPE), linear-low density polyethylene (LLDPE) and low-density polyethylene (LDPE). Certain synthetic polymers possess favourable mechanical properties, for example good tensile strength or high elongation. Additives, such as colouring agents, stabilisers or plasticisers, are often added to polymers during manufacture or processing, either to aid processing or to improve performance during use [4].

A shortcoming and significant drawback of synthetic polymers is that these materials are persistent in the environment. All polymers undergo degradation, even synthetic materials; the only variable is the rate of degradation which can lead to an enduring presence in the environment. Recalcitrant behaviour is attributable to properties such as hydrophobicity, high molecular weight, and the chemical and structural composition of the material. These polymers easily accumulate in the environment and can become hazardous to the ecology of the area. This is especially true for materials designed for one-time use such as food packaging, disposable cutlery, plastic bottles, and so on [3,7-9].

Changes in polymer properties due to chemical, physical or biological reactions resulting in bond scissions and subsequent chemical transformations are categorised as polymer ageing or degradation. These modifications cause the loss or alteration in material features such as mechanical properties, thermal or optical characteristics demonstrated by crazing, cracking, erosion, discoloration and phase separation. There are several classes of degradations which materials can undergo, for example, photo-oxidative, thermal, mechanical, catalytic and bio-degradation. The type of degradation is determined by the conditions to which the substance is exposed, such as elevated temperature, moisture and exposure to sunlight. Biological elements, such as bacteria and fungi, can also attack materials under certain conditions. The constituents of the material also has an effect on the ability of the material to degrade, for example the

presence of labile bonds in the polymer chain, or the inclusion of substances such as starch or proteins with higher rates of degradation [7-12].

The degradation of a polyolefin material, like polyethylene, consists of a two-step process, oxidation of the polyolefin followed by attack of micro-organisms to achieve bio-degradation. During oxidation, the alkane chains are oxidised to ketones which are then cleaved by hydrolysis to give the corresponding acid. This improves the hydrophilic nature of the polymer that promotes further hydrolysis of the polymer. The second step is known as biodegradation since the oxidation yields lower molecular weight products that can be degraded by the enzymes of microorganisms. Degradation of synthetic polymers can be influenced by the presence of stabilisers that inhibit deterioration. Recent studies have shown that the incorporation of natural fillers, such as proteins or plant fibres, can improve the degradability of synthetic polymers, especially since the inclusion enhances the hydrophilic properties of the material, which allows for hydrolysis and further oxidative attack [3,7,13-18].

Environmental conditions cause deterioration of polymeric material by means of hydrolysis, oxidation and photo-degradation. This initial degradation decreases the size of the polymer molecules to allow microbiological attack during biodegradation. Biodegradation or decomposition of the polymer is achieved by microorganisms such as bacteria and fungi that essentially digest and metabolise small molecules of the material to achieve mineralisation. The molecules should be of sufficiently low molecular weight since large polymer molecules cannot pass through the cell membrane of the microorganism [3,14,17,19,20]

There are polymers, derived from renewable biomass, that can be considered to be biodegradable, but these polymers do not occur without human intervention. Poly(lactic acid) (PLA) is an example of such a polymer. PLA belongs to the family of aliphatic polyesters derived from α-hydroxy acids (mainly starch and sugars). A more accurate description of PLA is a "bio-based plastic" since the monomers are produced through an industrial fermentation process. The thermal and mechanical properties of biodegradable polymers are normally not suited for the applications that synthetic polymers have been designed for, and bio-based polymers can be more expensive to manufacture [3,21,22].

Natural polymers are produced by living organisms but must be refined or processed before use. Examples of naturally occurring polymers are natural rubber, silk, wool, DNA, cellulose and proteins. Natural polymers are also known as biological polymers, or biopolymers. Compared to the simple, more random structure of synthetic polymers, biopolymers have complex molecular groupings of structures that adopt specific and well-defined shapes. The precision of the arrangement of the structures is ultimately what makes the molecules able to function in organisms. Natural polymers occur in a large variety of structures and compositions. These polymers are classified according to the nature of the repeating unit they are made of: (i) polysaccharides are made up of simple sugars, such as glucose; (ii) proteins are composed of amino acids; and (iii) DNA molecules consist of nucleotides, covalently bonded into nucleic acids. Biopolymers are capable of biodegradation, meaning that the polymer material is eventually broken down into carbon dioxide (CO_2), water (H_2O) and organic residues [11,23].

Blending of natural polymers with synthetic polymers can create novel materials and improve selected properties of the material, for example, the mechanical properties of the natural polymer are enhanced and the degradability of the synthetic polymer is augmented. Natural polymers occur in a large variety of structures and compositions, from proteins to polysaccharides and are readily acquired since they are abundant, widely available and a sustainable resource. All these factors combined effectively lowers the cost of acquisition [3,9,10,24-26].

Careless littering of plastic materials in particular and ignorance result in the accumulation of waste in the environment, which is not aesthetically pleasing and could become a health hazard for all life forms. As an alternative to the use of completely natural polymers, it has become popular to combine natural and synthetic polymers. These blends possess the functional properties of the synthetic polymers, with the added benefit of improved degradability due to the addition of the natural elements. Biodegradable polymers create the prospect of possible solutions to waste-disposal problems associated with traditional petroleum-based plastics. Biodegradation is dependent on the initial abiotic oxidation of the polymer that results from exposure to the elements, namely sunlight, wind, rain and elevated temperatures before micro-organisms can be effective. As a consequence of contact with the external environment, preliminary degradation produces lower molecular weight molecules that are more susceptible to microbial attack [7,24].

Water sensitivity of natural polymers

The hydrophobic or hydrophilic nature of a material will determine the extent to which water will be absorbed by the material. The structure of most natural polymers contains polar chemical groups, which makes these materials hydrophilic. A hydrophilic character promotes degradation, since hydrolysis can be a major feature in the degradation of polymeric materials [27].

Water can be absorbed by a polymer via diffusion during humid conditions or surface water resulting from rainfall or condensation. Absorption of water may result in swelling of the material. The presence of water initiates the hydrolysis of the polymer and rupturing of the polymer backbone that lead to the creation of oligomers and monomers. As degradation progresses, changes in the microstructure of the matrix occur due to the formation of pores. Lower molecular weight products can be released. The sensitivity of natural polymers to water can impede functioning and natural polymers are inclined to exhibit inferior mechanical properties [26,28-30].

Many polymer composites, when exposed to wet or humid environment, can absorb water with detrimental consequences. The absorbed water may affect the material by swelling (dimensional changes), reduction of the glass transition temperature (plasticisation), or reduction in physical or mechanical properties such as stiffness, strength or hardness. Diminished properties can also result from an interaction of any of the composite components with the absorbed water molecules. The amount of water absorbed is directly related to the amount of degradation that occurs due to hydrolysis. Hence, the rate of the degradation of materials such as synthetic polymers is improved [28].

1.3.2. Degradation of polymer materials

Polymer degradation is defined as a loss or change in the characteristic properties of a material. Degradation results from changes in the physical or chemical structure of the polymer due to

various external and internal factors, as described earlier. In some cases, degradation processes result in reduced molecular weight. Degradation can also be associated with the process of ageing. The exposure of a polymeric material to a certain environment over time is known as weathering of that material. Weathering can occur in a natural environment, such as outdoor conditions during use, or in a simulated environment, such as soil burial, UV radiation treatment or water submersion. The process in a simulated environment is termed artificial ageing or weathering. Environmental conditions that polymers are subjected to during the weathering period can result in changes in appearance, modified mechanical properties, and so on [6,31-33].

Ageing

According to the Oxford Dictionary, ageing is defined as the process of becoming older, or increasing in age. Ageing is the inevitable deterioration of the material structure and loss of functionality due to modified physical and/or chemical structure. This process is understood to involve changes in the properties of a material, either spontaneously or through deliberate action over a period of time. The adjective used to describe the degradation or ageing process explains the manner in which physical or chemical changes in the polymer can occur. For example, aqueous ageing arises due to the action of water or moisture on the polymer; oxidative degradation is caused by the action of an oxidising agent on a material, and the process that occurs when the polymer is in contact with soil is known as underground ageing. Physical ageing is a thermodynamic process that causes changes in the physical structure of polymers. Over time, short segments of the polymer chain are subjected to small-scale rearrangements that affect physical properties such as density, crystallinity and changes in dimensions. During use, molecular rearrangements resulting from applied stress cause certain polymers to undergo crazing. Crazing is the formation of cavities that look like cracks, but the gap between the surfaces of the cavity is linked by fibrils of the polymer. The size of a cavity is often smaller than a few micrometres. Initiation of crazes is influenced by increased tensile stress and factors in the material environment such as absorbed water that increases molecular mobility. A crack can be defined as the line where a material is broken but not separated. Stress cracking is defined as an external or internal crack in a material caused by tensile stress. This type of cracking usually entails brittle failure, and rarely involves the formation of fibrils that connect the failure surfaces. Stress cracking is often explained as slow crack growth, and the most well-known

type is referred to as environmental stress cracking (ESC). Environmental stress cracking is caused by the combined action of mechanical stress with chemical agents and/or radiation. It is believed that ESC is initiated at imperfections or impurities in the polymer structure. The environmental agent responsible for the initiation of the crack is indicated by the name given to the cracking process, for example oxidative cracking, UV cracking, etc. A material, exposed to conditions that facilitate an environmental factor to move down the length of the crack, will experience plasticisation of the high-stress region of the crack tip. Under continued stress, the crack will spread through the material, resulting in failure on [6,31-34].

Environmental degradation

In general, most synthetic polymers are inherently resistant to environmental factors, and hence, environmental degradation. For the duration or their use, polymer materials are exposed to environmental factors, which can adversely affect the properties of the polymer. Environmental degradation of polymers is the deterioration of polymer properties due to the action of environmental factors, such as heat, light, moisture, oxygen, or biological organisms. Polymeric materials susceptible to environmental factors are known as environmentally degradable polymers. Under environmental exposure, high thermal energy can cause depolymerisation; solar radiation can result in photo-initiated oxidation; the presence of water, under the right conditions, results in hydrolytic reactions; and exposure to ozone can produce free radicals. Consequently, the formation of smaller polymer fragments ensues, which facilitates the attack of biological organisms. Degradation that results from the action of biological organisms, naturally present in the environment, is known as biodegradation. Biological organisms that attack polymers, and cause depolymerisation, are known as depolymerases (Figure 1.1) [10,26,31,32].

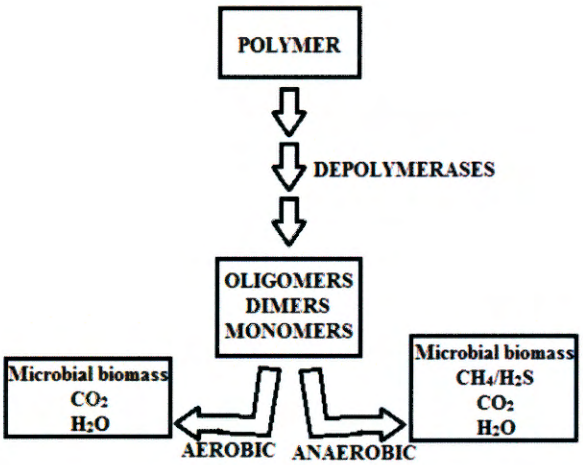

Figure 1.1 Schematic diagram of polymer degradation under aerobic and anaerobic conditions [7]

Additives that are able to improve degradation reactions are known as pro-degradants. These additives are usually added to polymers during the melt stage to increase the rate of oxo-degradation by improving the efficiency of reactions with atmospheric oxygen during functioning. Oxo-degradation proceeds via photo-degradation and oxidation reactions. Pro-degradant additives can be transition metal salt complexes or other transition metal free compounds that possess chromophoric groups. Transition metal ions, in their various forms, are the most extensively used pro-degradant additive. The decomposition of hydro-peroxides into free radicals is catalysed by transition metal complexes and the photo-sensitivity of the material is increased, which promotes UV degradation. Some of the most commonly used transition metals include iron, cobalt and manganese. Bloodmeal contains iron in the heme-complex present in blood. The heme-complex is fundamentally involved in the transport of oxygen and carbon dioxide in the blood of an organism. Proteins are linear polypeptide molecules with a precise length. A polypeptide chain comprises a distinct combination of twenty (20) covalently bonded amino acids. An understanding of the chemical reactivity of the amino acid functional groups is important because they provide many reaction sites for potential cross-linking or chemical grafting. Beef blood meal contains more lysine, threonine, valine, leucine, tyrosine, and phenylalanine while pork blood meal contains more histidine, arginine, proline, glycine, and isoleucine. Of these, cysteine and lysine are the most reactive amino acids [6,26,35].

Different analytical techniques can be used to estimate the extent of degradation in the material. Alterations in morphology such as increased surface roughness, etc., can be observed with

microscopic techniques. Changes in rheological properties such as altered crystal structure, etc., can be determined using mechanical testing, X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Chemical modifications of the material structure can be distinguished with spectroscopic methods, such as Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) and mass spectrometry (MS), etc. Gel permeation chromatography (GPC) can confirm changes in molecular weight of the material. Gravimetric measures can be employed to determine weight loss, but differences are often negligible and can be attributed to loss of volatile or soluble impurities [2,17,26,34].

Degradation of polymer waste through various means is one alternative to deal with the accumulation of waste material in the environment. Biodegradation of synthetic materials and the assimilation into the environment is the ultimate objective of research into sustainable substances.

1.3.3. Proteins: Classification and properties

Essential components in each living cell, proteins function as important structural components of skin, hair, muscle and nervous tissue. Proteins also serve biological functions in living organisms as enzymes and hormones. Proteins are natural polymers that can originate from both plant and animal sources, for example, soy proteins are extracted from plants and bloodmeal is derived from animal blood. The structures of proteins are divided into primary, secondary, tertiary and quaternary structures. The most basic components of proteins are amino acids. The general structure of an amino acid is shown in Figure 1.2. The primary structure is the order in which the amino acids are joined to form the polypeptide chain. The specific amino acid sequence is determined by the genetic code of the organism. An amino acid is made up of an amino group, a carboxyl group and a side chain, or "R group".

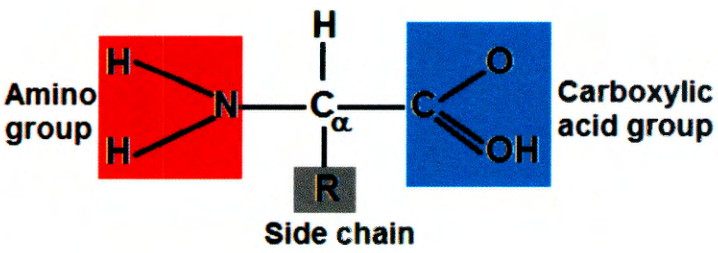

Figure 1.2 General structure of an amino acid [36]

These "R groups" can impart specific characteristics to the amino acid, for example hydrophilic or hydrophobic behaviour. Amino acids can be considered as the 'building blocks' of proteins, as monomers are the constituent parts of a polymer. There are twenty known structures of amino acids, as shown in Table A.1.1 in the Appendix [36].

1.3.4. Proteins as materials

Substantial quantities of animal derivatives from livestock, bred for meat, dairy and eggs, is wasted because these parts of the animal are not fit for human consumption. Unused animal products, such as rawhide, bone, blood and other tissues, are subjected to rendering processes resulting in many useful products. Rendering involves both chemical and physical modification of the substance to generate or convert the protein in a usable form. The rendering industry provides an assortment of useful products of animal origin such as bloodmeal, bone meal, feathermeal, fishmeal, meat meal, and poultry meal. These products were previously used as animal feed, but are currently used mostly as fertilisers. If the animal products are not processed by the rendering industry, an accumulation of animal derivatives could hinder the meat industry, intensify environmental pollution and present a potential hazard to human and animal health [37-39].

Research focused on the development of sustainable materials to replace synthetic plastics has explored protein-based plastics. Proteins originate from renewable resources as derivatives from agricultural practices, and most importantly, proteins are biodegradable or compostable. This is beneficial from an environmental and economic perspective. In general, proteins consist of approximately 100-500 amino acid residues covalently bonded in a polypeptide chain. Each protein of a particular type has a characteristic amino acid sequence; subsequently there exists a considerable assortment of proteins. In addition, various interactions take place between amino acid residues of a polypeptide chain, between individual polypeptide chains and between whole proteins. Materials produced from proteins accordingly possess a wide range of properties [38,40,41].

Present in all living cells, protein substances are widely varied and can be recovered from many resources as by-products or wastes of the agricultural and horticultural industries. The proteins

must often be removed or extracted from plant or animal tissues. Abundant proteins such as soy from plants, and proteins such as gelatine or bloodmeal from animals, have been manufactured into plastics with reasonable properties. Soy protein is extracted as a by-product from soybeans and was one of the first biopolymers from agriculture used for the manufacture of moulded materials. Soy protein plastics are brittle and require plasticisers for improved mechanical properties. Some components of Ford cars were manufactured with a phenol-formaldehyde/soybean flour mixture in the 1930s although, due to the expense of extracting the proteins and progress in the development of synthetic plastics, this practice was stopped [11,40,42-44].

A protein, in its native form, exists in a folded conformation stabilised by hydrophobic interactions, hydrogen bonding, and electrostatic interactions between amino acid functional groups. These interactions between the components of proteins must be disrupted before the proteins can be efficiently processed into a material. Proteins are sensitive to changes in temperature and pH which can rupture low-energy intermolecular bonds that stabilise the protein; this is known as denaturation of the protein. Denaturation of the protein serves to disentangle and uncoil the protein structures. The disruption of the interactions and bonds between the amino acids of the polypeptide chain allows new interactions to form during processing. Once the protein has been denatured, the polypeptide chains can rearrange into a three-dimensional structure, stabilised by interactions between the protein components. Production of protein-based materials typically makes use of either wet processes, e.g. casting, or dry processes, such as extrusion. Each technological process is dependent on the specific properties of the protein. The complicated nature of proteins thus limits possible processing conditions [12,39,40,45].

The most important aspect of materials produced from proteins is that the materials can be composted or can be considered as biodegradable. The proteins are derived from renewable resources, which aid the economical sustainability of the product. These materials could be applied in the packaging industry where the plastic material is usually disposed of after a single use.

Plastic materials derived from proteins usually possess inferior mechanical properties such as reduced flexibility and brittle behaviour. For this reason, several researchers have investigated

the incorporation of various additives, such as plasticisers, to improve these properties. A balance between improving the performance of the material with the addition of chemicals, and the inherent biodegradable character of the material must be maintained [41,46].

An alternative to the addition of chemicals to the material is to produce composites of natural and synthetic polymers, such as polyethylene (PE) with bloodmeal. The polymers are mixed to obtain a trade-off of beneficial properties, such as the functional mechanical properties of polyethylene with improved degradability [24,47].

1.3.5. Bloodmeal

Blood is classified as a specialised kind of connective tissue and serves many vital roles in an organism. The main component of blood is water, better known as blood plasma. The rest of the constituents are suspended in the plasma. Typical elements of blood are red blood cells (erythrocytes), white blood cells (leukocytes), plasma proteins, platelets, hormones, enzymes, nutrients, gases, and wastes. Each component serves a critical function and the blood, in its entirety, serves various regulatory roles in the organism. The erythrocytes comprise the majority of the solid components of blood. Blood possesses a higher concentration of iron than the flesh of an animal. The iron, present in the haemoglobin sub-units of erythrocytes, functions to bind molecular oxygen that enters the vessels of the lungs during inhalation, and conveys it to the body tissues by means of the circulatory system. Iron in the haemoglobin complex is also responsible for the red colour of blood, since the iron oxidises in air, which gives blood its red hue. Bovine blood is composed of approximately 80% water, 15% protein, 5% nutrients, gases and wastes. The amino acid content of bloodmeal is tabulated in Table A.1.2 in the Appendix [30,48].

In 2010/11, roughly 3-million head of cattle were slaughtered in South Africa for commercial markets or for small enterprises. There is considerable consumption of beef and veal in South Africa [49]. Slaughterhouses and rendering plants typically dispose of the blood produced from slaughtering cattle *via* incineration, to produce blood-char, or through drying, to produce bloodmeal. Essentially, bloodmeal is the components of blood with the plasma, or water, removed. Bloodmeal is a dry, inert powder which is currently used as a high-nitrogen fertilizer. The use of bloodmeal as a high protein addition to animal feed was prohibited due to the

outbreak of the Aphtae epizooticae (foot-and-mouth) disease in cattle. It is one of the highest non-synthetic sources of nitrogen. A renewable source of protein is therefore available and recent research has investigated bloodmeal-based thermoplastics and their properties [24,46,47,50].

1.3.6. Bloodmeal-based thermoplastics

At the University of Waikato in New Zealand, researchers have done extensive studies on the production of bloodmeal-based thermoplastics. They have shown that bloodmeal can be extruded and injection moulded for various applications when bloodmeal is treated with denaturants, reducing agents and plasticisers. Each chemical additive has a specific effect on the protein during processing; these additives thus also influence the properties of the resulting thermoplastic. Examples of chemicals that act to denature protein molecules are sodium dodecyl sulphate (SDS) and urea. The protein must undergo denaturation for the protein-protein interactions to be disrupted. The reducing agent, sodium sulphate, serves to cleave covalent cross-links of the bloodmeal proteins, facilitating processing. The action of the reducing and denaturing agents allow new interactions to form between molecules. Water is a low molecular weight molecule with a sufficiently high boiling point, which serves as a plasticiser in bloodmeal-based thermoplastics, improving processability [43,46,50-53].

1.3.7. Bloodmeal-filled polymers

Blends and composites of bloodmeal with synthetic polymers, such as UHMWPE, LLDPE, and polybutylene succinate (PBS), have been the topic of various studies in previous years. Early research has shown that the interfacial adhesion between the matrix and filler was inadequate and required the use of chemical additives to enhance compatibility between the phases. Evidence of the poor adhesion was the noteworthy decrease in mechanical properties for materials without additives. The incompatibility of the blend is mainly due to the hydrophobic nature of synthetic polymers and the hydrophilic nature of bloodmeal. Incompatibility of the constituents was also evident in morphological observations since blends without additives displayed phase separation. In studies that exercised contact angle measurements, the materials with increased bloodmeal content presented an increased hydrophilic nature, although this was not true for blends containing compatibiliser. Similarly, water absorption experiments showed

improved water absorption for blends containing bloodmeal compared to the neat polymer. Investigations of thermal properties of proteins indicated that the proteins could be processed using traditional processing methods [24,54,55].

1.4. Objectives of this study

The present work aims to produce polyethylene-bloodmeal (BM) composites with HDPE. The thermal behaviour was determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The mechanical properties of the composites were studied using tensile testing. The effect of the addition of bloodmeal on the environmental degradation of HDPE was investigated. Morphology of the aged samples was examined with attenuated total reflectance (ATR)-FTIR spectroscopy, optical microscopy and scanning electron microscopy (SEM).

1.5. Thesis outline

The outline of this thesis is as follows:

Chapter 1: General introduction and literature review
Chapter 2: Materials and methods
Chapter 3: Results and discussion
Chapter 4: Conclusions

1.6. References

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Chapter 2

Materials and Methods

2.1 Materials

2.1.1 High-density polyethylene (HDPE)

HDPE was supplied in pellet form by Safripol Pty. Ltd. from Sasolburg, South Africa. It has a density of 0.956 g cm^{-3} and a crystalline melting range of 130-133 °C. It shows a tensile yield strength of 27 MPa, an ultimate tensile strength of 38 MPa, and ultimate elongation values can be greater than 600%.

2.1.2 Bloodmeal (BM)

Bloodmeal was received from Comchem Trading subsidiary, TALCHEM. The following specifications were supplied:

Table 2.1 Information received with bloodmeal

Content	Proportion / g kg^{-1}
Protein	750 (min)
Phosphorous	2 (min)
Fat	60 (min)
Fat	80 (max)
Calcium	5 (max)
Moisture	100 (max)

During bloodmeal production, the proteins are treated at elevated temperatures for the elimination of pathogens and the removal of water. Increased temperature conditions also result in cross-linking between reactive proteins, which hinders further processing without the addition of chemicals [1]. We did not use chemical additives, and we did not process the bloodmeal before use.

Thermogravimetric analysis (TGA) analysis of bloodmeal showed the initial mass loss to occur around 100 °C, and this was attributed to the removal of water. Further mass loss from approximately 200 °C is believed to result from the rupture of peptide bonds of the protein molecule [2]. Our tests showed similar results.

2.2 Sample preparation

The bloodmeal powder was sieved using a stainless steel King Test Laboratory Test Sieve with an aperture size of 600 μm. Before mixing, the bloodmeal was placed in an oven at 80 °C overnight to remove any absorbed water and kept at 40 °C until all composites of polyethylene and bloodmeal had been prepared. A colour change from brown to dark brown was observed after the bloodmeal was placed in the oven. Samples were prepared according to the weight percentages in Table 2.2.

Table 2.2 Table of composite proportions

Weight % HDPE	Weight % bloodmeal
100	0
99	1
95	5
90	10
80	20

The HDPE pellets were used directly from the bag without drying. The HDPE-bloodmeal composites were prepared by a melt mixing process using a Brabender PLASTICORDER PL 2100 at 150 °C. The mixing was done at a speed of 30 rpm, and the dried bloodmeal was added after a minute and allowed to blend for a total of 10 minutes.

Thin films with thicknesses of approximately 0.2, 0.7 and 1.0 mm were prepared for each composition. The material was placed on the melt press at 180 °C, allowing the material to melt while gradually increasing the applied pressure. After 5 minutes, the pressure was increased to 50 bar for an additional 5 minutes.

2.3 Characterisation techniques

2.3.1 Moisture content

The moisture content of the composites had to be determined to verify the effect of the addition of bloodmeal to polyethylene in terms of moisture content. The presence of bloodmeal in HDPE was expected to increase the moisture content of the composites to some extent.

Moisture content of the samples was determined gravimetrically by weighing bloodmeal powder and pieces of composite material (average weight of approximately 1 g, $M_{initial}$), followed by drying (M_{dry}) in an air-circulating oven at 80 °C over-night (± 24 hours). Moisture content of the 0.2 mm composite films were tested for each composition. An average of three specimens were tested. The percentage moisture content was calculated with Equation 2.1 [3].

$$\left[\%\ \text{Moisture content} = \frac{M(\text{initial}) - M(\text{dry})}{M(\text{initial})}\right] \times 100\% \qquad (2.1)$$

2.3.2 Water absorption

The purpose of the water absorption testing was to show whether the presence of bloodmeal in polyethylene improved the water absorption of the composites. Improved absorption of water enhances the prospect of hydrolytic degradation in the material.

The ability of the material to absorb water was investigated by cutting 15 x 15 mm samples (average weight of 0.42 g). The samples were weighed ($M_{initial}$) and then immersed in 100 ml deionised water at room temperature. Surface water was removed from the blends using a paper towel before re-weighing (M_{wet}) after 48 hours submersion in deionised water.

For testing the water absorbance of pure bloodmeal, approximately 1 g ($M_{initial}$) was weighed and placed in an oven at 80 °C overnight. The dried bloodmeal was then placed in a desiccator to cool for an hour. Once cooled, the bloodmeal powder was mixed with 100 ml deionised water and left at ambient temperature for 48 hours. The bloodmeal was filtered under vacuum using a Büchner funnel before re-weighing (M_{wet}) at ambient temperature.

The difference between the initial mass ($M_{initial}$) and the mass after immersion (M_{wet}) was used to calculate the percentage water absorption using Equation 2.2.

$$\text{Percentage water absorption} = \frac{M(wet) - M(initial)}{M(initial)} \times 100 \qquad (2.2)$$

An average of three specimens were tested.

2.3.3 Underground ageing test

The aim of the underground ageing test was to simulate natural weathering conditions to test whether the addition of bloodmeal influenced the degradation of HDPE, and therefore the temperature and humidity were not controlled in these tests.

Samples of varying thickness (~0.2, 0.7, and 1.0 mm) were buried vertically in soil for 36 weeks. Approximately 500 ml of water was added to the soil every week and the humidity of the soil was monitored using a Major Tech MT662 Thermo-hygro humidity meter.

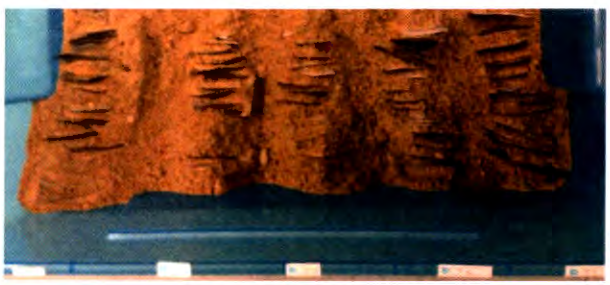

Figure 2.1 The positioning of composite samples in soil for the underground ageing test before covering with soil

A set of composite films were removed from the soil after four weeks, and then every eight weeks after that for a total of 36 weeks. Excess soil was wiped from the surface of the films, which were then rinsed with deionised water and dried with a paper towel. The films were left at ambient temperature for 24 hours before the films were characterised. Observations of the characterisations were correlated with ageing processes.

2.3.4 Differential scanning calorimetry (DSC)

The thermal transitions that a material undergoes during heating or cooling processes can be studied using a DSC. These thermal transitions, such as melting during heating, or crystallization during cooling, can provide valuable information about the material being tested. Clearly modified thermal transitions evident in thermal traces could lead a researcher to expect changes in other characteristic properties of the material in question. For example, changes in the crystal structure that can result from the incorporation of filler substances can alter the mechanical properties of a material [4].

DSC analyses were performed in a Perkin-Elmer DSC 6000 differential scanning calorimeter in flowing nitrogen atmosphere (20 ml min^{-1}). The samples having masses of 6-7 mg each were sealed in aluminium pans and heated from 0 to 200 °C, cooled from 200 to 0 °C and reheated from 0 to 200 °C at a rate of 10 °C min^{-1}. Three samples from each composition were analysed. Only the second heating scan was used to determine the melting enthalpies and temperatures. The crystallization enthalpies and temperatures were determined from the cooling scan.

2.3.5 Thermogravimetric analysis (TGA)

TGA is a technique which follows the mass of the sample as a function of temperature or time, under controlled conditions. The thermal trace, recorded as mass percentage versus temperature or time, supplies information regarding the thermal stability, decomposition and degradation temperatures, and the moisture or volatile content of the material under the specified conditions.

A Perkin Elmer STA 6000 simultaneous thermal analyser was used to study the influence of the addition of bloodmeal on the thermal stability of polyethylene. Samples with masses of 22 mg were heated from 25 to 600 °C at a heating rate of 10 °C min^{-1} and a nitrogen flow rate of 20 ml min^{-1}. TGA was done on all the compositions of the unaged composite samples, bloodmeal, HDPE, and 20% BM containing samples aged underground for 36 weeks. The analyses were performed in triplicate for each composition and ageing time, and the average values and standard deviations are reported.

2.3.6 Fourier-transform infrared (FTIR) spectroscopy

FTIR spectroscopy is a simple characterisation technique that provides useful information about the sample being examined. Chemical bonding and molecular structure can be investigated using the principle that molecules in a sample vibrate at a distinctive frequency when irradiated with infrared (IR) light. Particular bonds in certain molecules provide a characteristic spectrum, allowing specific chemical groups to be identified in a material. The technique is non-destructive, and only very small amounts of the material are required for analysis, which is ideal when working with a limited amount of sample.

A PIKE Miracle$_{TM}$ ATR, with a diamond crystal, connected to a Perkin-Elmer Spectrum 100 FTIR spectrometer, was used for the examination of the composites. A clean, empty diamond crystal was used for the collection of the background spectrum. The ATR-FTIR spectra were recorded between 4000 and 650 cm^{-1} at a resolution of 8 cm^{-1}.

The carbonyl index can be used as a measure of the extent of oxidation of a material. Calculation of the carbonyl index is achieved by taking the ratio of the carbonyl absorbance to the distinctive C-H stretching absorbance at 1465 cm^{-1}. In an FTIR spectrum, carbonyl groups are observed in the 1680-1850 cm^{-1} range. A broad peak in this range can indicate the presence of different oxidised groups due to the overlapping bands of the carbonyl groups. The carbonyl index of the composites was followed to verify whether oxidation processes had occurred during the underground ageing study [5,6].

2.3.7 Optical microscopy

Microscopy techniques, such as optical microscopy and scanning electron microscopy (SEM), are often used to observe and investigate the morphology of samples. Optical microscopy was implemented to distinguish the overall dispersion of bloodmeal in HDPE; therefore the films were not examined at high magnifications.

Optical microscopy was performed using a Zeiss microscope at 20x magnification. The 0.2 mm films and the 1.0 mm films of all the compositions were examined for unaged films and films

aged underground for 36 weeks. An AxioCam ERc5s camera, connected to the microscope, captured the pictures using Zeiss software.

2.3.8 Scanning electron microscopy (SEM)

SEM is a technique used to investigate the morphology of a sample. An electron beam is generated in the microscope, which is then guided down the microscope column to the sample situated on the stage, under vacuum. Once the primary electrons of the electron beam collide with the particles of the sample, the electrons are scattered and travel on a new trajectory. An incident electron can be scattered in different ways, depending on the interaction with the sample, and specific detectors are used to detect and interpret these signals to provide information about the sample surface. The SEM can record images at very high magnifications. SEM images are useful for observing the topography of a sample, for determining the dispersion of filler particles in a polymer matrix, identifying phase separation in a polymer blend and visualisation of the interaction between composite components [7].

A Tescan VEGA 3 SEM with a secondary electron detector was used to acquire the images of the composites. The surfaces of the samples were coated with carbon before examination to provide a conductive surface for the imaging to occur. Images were taken at 51, 100, and 200 times magnification and a voltage of 20 kV.

2.3.9 Tensile testing

Depending on the interactions between the filler and the polymer matrix, the mechanical properties of a composite can vary from that of the pure substance. Variations in the mechanical properties can give some insight into the anticipated effect of a specific treatment on a material. Reported outcomes of underground ageing on polymer materials include increased modulus and yield stress, as well as decreased elongation at break values. Ageing processes involve abiotic and biotic reactions. Abiotic reactions, such as oxidation, typically precede biotic processes, such as biodegradation. Synthetic polymers, with high molecular weight components, usually require extended periods of time before biodegradation will occur.

The tensile testing was performed on a Hounsfield H5KS universal tensile testing machine. A minimum of six dumbbell-shaped samples were tested for each composition, for each film thickness, for every ageing time, and the average results are presented. The dimensions of the dumbbell-shape are indicated in Figure 2.2.

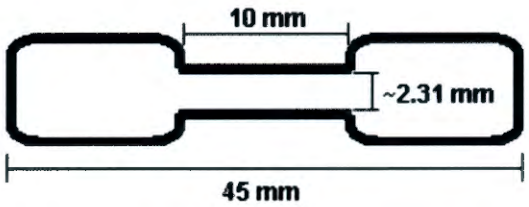

Figure 2.2 Dimensions of the dumbbell-shape used for tensile testing

Young's modulus was calculated from the initial part of the stress-strain curve (within 1.8% strain) for all the films, at each ageing time. The stress at yield and elongation at break values were determined by reading the values off the stress-strain curves for all the composites. The changes in the above properties were followed to detect the influence of soil burial on the materials over time.

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Chapter 3

Results and Discussion

3.1.1 Moisture content

The moisture content of pure bloodmeal and the HDPE/BM composites was determined using the method described in Section 2.3.1. The difference in the mass measured before and after exposure to heat in the oven can be thought of as the amount of moisture released from the sample.

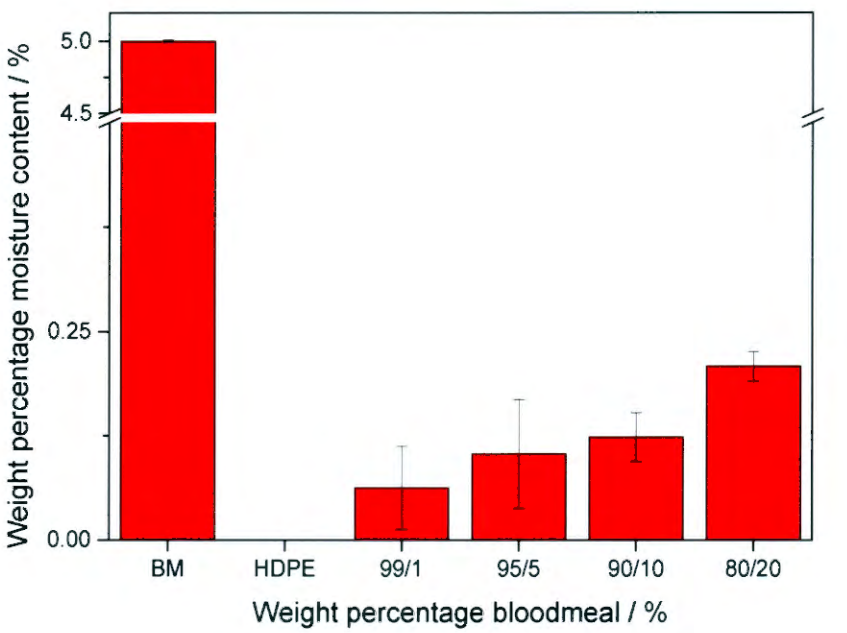


Figure 3.1 Moisture content of pure bloodmeal powder and of HDPE/BM composites prior to underground ageing stored at room temperature

Pure HDPE is inherently hydrophobic and does not absorb water, neither does it release any moisture. Given that pure bloodmeal powder released approximately 5% moisture (Figure 3.1), it was expected that the bloodmeal contained in the polymer would emulate this behaviour. It can be seen that the moisture content increases with the amount of bloodmeal in the composite.

Experimental results showed that 99/1 HDPE/BM composite released slightly more moisture than predicted. A possible explanation for this observation is that mixing the hydrophilic bloodmeal with the hydrophobic HDPE could have forced the minor phase, with very low content, to the surface of the polymer film, thereby maintaining a mostly hydrophobic core. The bloodmeal particles that would be exposed at the surface of the polymer and could release any moisture bound to the bloodmeal particle. Conversely, for the 5, 10 and 20% bloodmeal containing composites, the moisture released was less than expected. As the bloodmeal content increased, the hydrophilic particles could cluster together in the bulk of the film. Since the HDPE enveloped the bloodmeal particles, a barrier was formed, preventing the escape of moisture.

It was shown that bloodmeal powder naturally contained some moisture (as seen in Table A.3.1 in the Appendix). When mixing bloodmeal powder with HDPE, the expected amount of moisture was not released, so the moisture present in the bloodmeal had been retained in the polyethylene/bloodmeal composite. These results indicate that the addition of bloodmeal to HDPE can increase the moisture content of the resulting composite to some extent. The increased moisture contained in the composite could promote hydrolytic degradation of the material.

3.1.2 Water absorption

The water absorption of pure bloodmeal and the HDPE/BM composites was determined as described in Section 2.3.2. It was confirmed that the films that did not contain bloodmeal did not absorb any water since polyethylene does not possess any hydrophilic groups. Water can only be absorbed by the composite if the bloodmeal particles are localised on the surface of the film, thus an approximation of the amount of bloodmeal particles exposed on the surface of the films was made. An estimation of water absorption per composite was based on the amount of bloodmeal present in the composite, assuming that all the bloodmeal particles in the sample could absorb water. A comparison of these estimated values with the experimentally determined values indicated that the bloodmeal was not uniformly distributed in the HDPE films. The values varied with thickness and with bloodmeal content, as shown in Table 3.1.

Water absorption of the composites was expected to decrease as the film thickness increased. This trend was observed for the HDPE/BM 90/10 composite films. It was also expected that films containing a higher weight percentage of bloodmeal would absorb more water. This was only partially observed. For the 0.2 mm thick films, the bloodmeal particles were most likely situated completely on the surface of the polymer, especially at high content. Considering that the adhesion between the filler and matrix was probably not optimal (because the polymer is hydrophobic and bloodmeal is hydrophilic), a surface particle could easily become dislodged from the polymer matrix, thus negatively affecting the ability of the composite to absorb water.

Table 3.1 Water absorption for pure HDPE, as well as the 90/10 and 80/20 w/w HDPE/BM composite films prior to underground ageing

Sample	Film thickness	Water absorption / %	Expected water absorption / %	Estimated % of BM exposed on film surface
Bloodmeal	-	78 ± 0	-	-
HDPE	0.2 mm	0	0	-
HDPE	1.0 mm	0	0	-
90/10 w/w HDPE/BM	0.2 mm	1.7 ± 0.0	7.8	22
90/10 w/w HDPE/BM	1.0 mm	0.7 ± 0.0	7.8	9
80/20 w/w HDPE/BM	0.2 mm	1.2 ± 0.0	15.6	8
80/20 w/w HDPE/BM	1.0 mm	1.9 ± 0.0	15.6	12

Bloodmeal has demonstrated an affinity for water, and is able to absorb large amounts of water, even under ambient conditions. This could be beneficial in a humid composting environment to aid the degradation of the bloodmeal proteins [1,2].

Although bloodmeal has a highly hydrophilic nature, it appears as if the incorporation of bloodmeal powder in HDPE does not significantly enhance the ability of the material to absorb water. The opposing characteristics of the matrix and filler, regarding the hydrophobicity of

HDPE and the hydrophilicity of bloodmeal, give rise to the varying distribution of the components within the composite. As the major phase of the composite, HDPE surrounds and covers the bloodmeal particles, especially in thicker films. This isolates the particles and prevents interaction with water or the environment. The composites can absorb only small amounts of water since some of the bloodmeal particles could be positioned exposed, on the surface of the film.

The fact that only limited amounts of water are absorbed could be beneficial during the life cycle of the material. Initially, the service life of the material is not drastically shortened since the material properties are largely preserved. When the time comes to discard the material, under the right conditions, hydrolytic degradation initiated by absorbed water can potentially contribute to the degradation processes [3–5].

3.1.3 Differential scanning calorimetry (DSC)

The DSC was used to study the influence of the addition of bloodmeal and environmental ageing on the melting and crystallization of HDPE. It was important to establish whether the bloodmeal particles would disrupt the crystal structure of HDPE, since this would ultimately affect the mechanical properties of the material.

As can be seen in Figure 3.2 and 3.3, the melting and crystallization peaks did not shift with increasing bloodmeal content. It can be inferred that the inclusion of bloodmeal in HDPE does not have an observable effect on the crystal structure of the polymer.

Table 3.2 shows the results obtained from the DSC analyses of the different composites. The melting temperatures did not change significantly with an increase in bloodmeal content or with extended ageing time. Similarly, during cooling, the crystallization temperatures also displayed very little variation with either composition or ageing time.

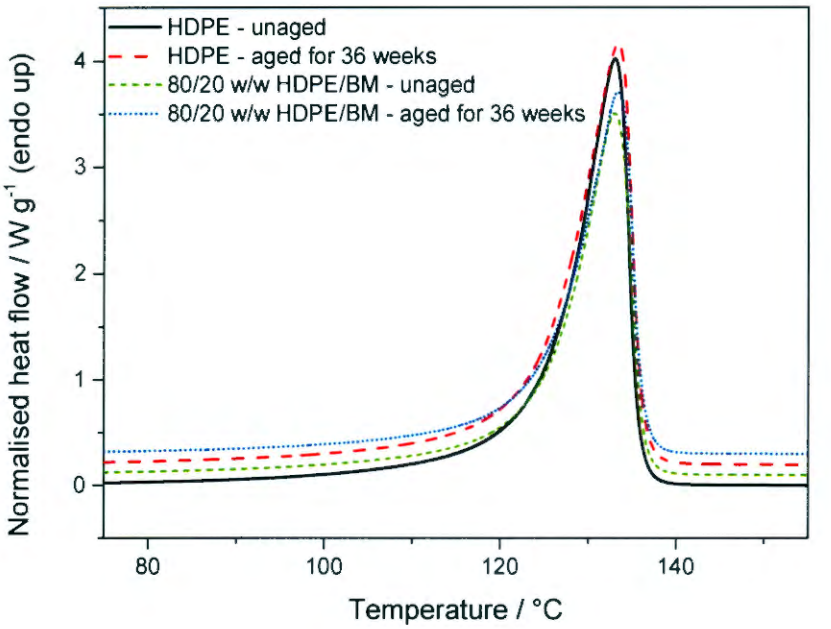


Figure 3.2 DSC second heating curves of HDPE and 80/20 w/w HDPE\BM composites prior to underground ageing and after underground ageing for 36 weeks

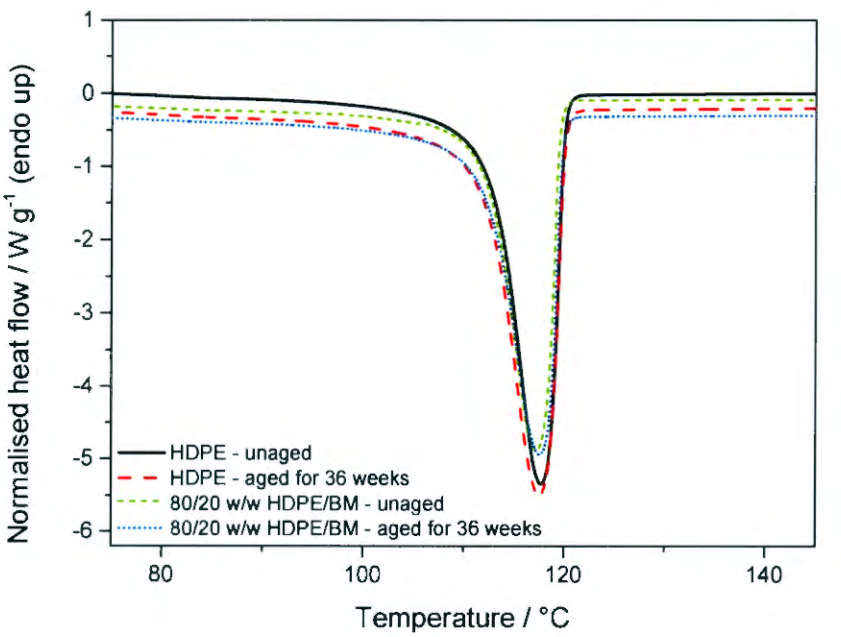


Figure 3.3 DSC cooling curves of HDPE and 80/20 w/w HDPE/BM composites prior to underground ageing and after underground ageing for 36 weeks

Table 3.2 Melting and crystallization temperatures and enthalpies obtained from the cooling and second heating curves for all the composites prior to underground ageing and after underground ageing for 36 weeks (1 mm thick samples)

HEATING				
Sample		**T_m / °C**	**ΔH_m / J g^{-1}**	**ΔH_m^{norm} / J g^{-1}**
Unaged	Pure HDPE	133.2 ± 0.2	198.3 ± 5.5	198.3 ± 5.5
	99/1 w/w HDPE/BM	133.2 ± 0.2	199.4 ± 4.6	201.4 ± 4.6
	95/5 w/w HDPE/BM	133.5 ± 0.4	200.0 ± 7.2	210.5 ± 7.6
	90/10 w/w HDPE/BM	133.0 ± 0.4	177.7 ± 11.6	197.4 ± 12.9
	80/20 w/w HDPE/BM	132.7 ± 0.2	159.8 ± 8.5	199.8 ± 10.7
Aged underground for 36 weeks	Pure HDPE	133.4 ± 0.1	198.1 ± 5.4	198.1 ± 5.4
	99/1 w/w HDPE/BM	133.2 ± 0.2	194.6 ± 6.0	196.5 ± 6.1
	95/5 w/w HDPE/BM	133.5 ± 0.3	187.6 ± 3.9	197.5 ± 4.1
	90/10 w/w HDPE/BM	133.5 ± 0.7	181.0 ± 20.5	201.1 ± 22.8
	80/20 w/w HDPE/BM	133.3 ± 0.3	183.1 ± 10.0	228.9 ± 12.4
COOLING				
Sample		**T_c / °C**	**ΔH_c / J g^{-1}**	**ΔH_c^{norm} / J g^{-1}**
Unaged	Pure HDPE	117.6 ± 0.4	-191.7 ± 9.2	-191.7 ± 9.2
	99/1 w/w HDPE/BM	118.0 ± 0.2	-168.1 ± 25.7	-169.8 ± 26.0
	95/5 w/w HDPE/BM	117.6 ± 0.2	-164.2 ± 5.7	-172.8 ± 6.0
	90/10 w/w HDPE/BM	117.8 ± 0.4	-155.2 ± 3.9	-172.4 ± 4.3
	80/20 w/w HDPE/BM	117.7 ± 0.2	-148.3 ± 5.2	-185.4 ± 6.5
Aged underground for 36 weeks	Pure HDPE	117.6 ± 0.3	-192.6 ± 14.8	-192.6 ± 14.8
	99/1 w/w HDPE/BM	118.0 ± 0.2	-168.0 ± 31.1	-169.7 ± 31.4
	95/5 w/w HDPE/BM	117.7 ± 0.3	-169.3 ± 7.8	-178.2 ± 8.2
	90/10 w/w HDPE/BM	117.5 ± 0.8	-171.7 ± 14.4	-190.8 ± 16.0
	80/20 w/w HDPE/BM	117.3 ± 0.2	-181.6 ± 13.6	-299.9 ± 16.9

T_m = peak temperature of melting; ΔH_m = melting enthalpy; T_c = peak temperature of crystallization; ΔH_c = crystallization enthalpy; ΔH_m^{norm} and ΔH_c^{norm} = enthalpies normalised with respect to the amount of HDPE in the sample.

The calculated enthalpy values were normalised with respect to the amount of HDPE in the samples. Comparison of the normalised enthalpy values for pure HDPE, unaged and aged underground for 36 weeks, shows that ageing processes did not have any effect on the crystal structure of the pure polymer. For the composites containing 1 and 5% bloodmeal, the enthalpy decreased slightly for the aged sample, but it increased slightly for the 90/10 HDPE/BM composite, and significantly for the 80/20 HDPE/BM composite. This indicates an increase in total crystallinity of the HDPE in the samples [6]. It has been shown by a number of authors that the degradation of polymeric substances is initiated in the amorphous parts of the material [7,8]. It can therefore be concluded that the observed increase in crystallinity resulted from recrystallization of the amorphous phase induced by ageing and the presence of BM particles.

The crystallization enthalpy values of all the composites correspond well with the melting enthalpy values, which is what one would expect. The heating and cooling curves of all of the composites can be found in the Appendix.

3.1.4 Thermogravimetric analysis (TGA)

The TGA curves of the unaged HDPE, bloodmeal, and HDPE/BM composites are shown in Figure 3.4. HDPE degrades in a single degradation step from approximately 455 °C. The two-step degradation of pure BM can be attributed to the loss of water between 100 and 200 °C, and the degradation of the protein structure of BM between 275 and 320 °C [9,10]. The average BM residue at 600 °C was 29.4%. Essentially, char is sample content that cannot be dissociated into smaller volatile fragments at the highest temperature of the specific thermogravimetric analysis test. The discussion that follows is an explanation of the possible constituents of the BM char.

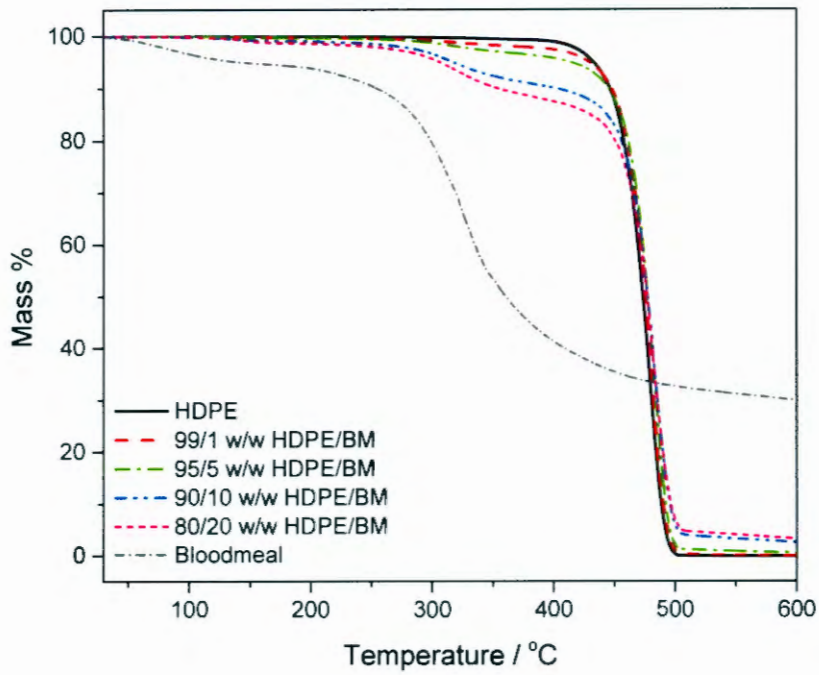


Figure 3.4 TGA curves of unaged bloodmeal, pure HDPE and the HDPE/BM composite films prior to underground ageing

Blood is made up of two main components, namely the blood plasma (~80%) and the cellular fraction which contains fat, carbohydrates and minerals (~20%). Blood plasma consists mostly of water (~90%), while plasma proteins make up the remainder. Most of the water is removed from the plasma during the spray drying process of bloodmeal production. Since the plasma component also contains proteins, when plasma is dehydrated, the residual proteins, minerals and fat can contribute to the cellular fraction of the bloodmeal. It has been reported that once dehydrated, the remaining plasma components can retain about 7% moisture, which works out to approximately 5.6% of the total mass of blood [11,12]. This value correlates well with the value determined for pure BM in the moisture content experiment in this study. From the TGA curve for BM, the mass lost at 200 °C was approximately 6%. This is attributed to loss of moisture from the sample, which also correlates with the reported moisture content values. The combined fat and carbohydrate content of blood constitutes 0.3%, while the mineral content amounts to just more than 0.6% of the cellular fraction of the blood. The remaining constituent of the cellular fraction are proteins (~17%) that are made up of amino acids [11]. The elements present in amino acids are mainly carbon, hydrogen, nitrogen and oxygen. The nitrogen present

in amino acids could contribute to the char content if the atoms recombine under the high heat conditions to form inorganic compounds, such as ammonium nitrites or nitrates. Similarly, recombination of carbon atoms to form carbides, carbonates, and cyanides (CN), all of which are considered to be inorganic, could marginally contribute to some char formation [13–15]. Certain amino acids, such as cysteine and methionine, are known to contain sulphur (amino acid structures are available in the Appendix). Using values from literature, the sulphur-containing amino acids of a protein sample could be equivalent to approximately 1.7% [16]. The amount of sulphur in a protein sample containing cysteine and methionine is considerably lower than about 0.06%. Thus, it is improbable that the presence of sulphur will affect the inorganic content of the protein sample to a noteworthy extent.

Considering all of the above information, the maximum possible char content for pure BM could be equivalent to approximately 20%, which is lower than the observed char content. A feasible explanation for this result is the addition of additives to the blood before or during processing. An example is sodium citrate which acts as an anti-coagulant during the spray-drying process, acids and sequestering agents may also be used to aid processing [12,17]. Added chemicals were not specified by the supplier of the bloodmeal, and attempts to find relevant information were not successful. In conclusion, the observed high char residue could have resulted from the presence of inorganic compounds added to the BM during processing, or compounds that formed during the analysis. It is also possible that the residue was sample matter that was not burnt off under the analysis conditions and temperature.

The TGA analysis of unaged HDPE shows the expected curve with a single degradation step (Figure 3.5). The degradation curve of HDPE aged underground for 36 weeks is virtually identical to that of the unaged HDPE. This shows that the period of underground ageing had no discernible effect on the pure HDPE films. The HDPE/BM composites displayed three degradation steps (Figures 3.4 and 3.5). The initial degradation was between 100 and 250 °C. The mass loss at 250 °C is approximately 1.9 and 2.7% of the unaged and aged 80/20 w/w HDPE/BM composite samples, respectively. These results support the results for the water absorption tests and show that it is possible that more BM is exposed on the film surface of the aged samples, thus more moisture was absorbed by the aged composite. It is conceivable that if BM particles were situated very close to the film surface, with only a thin coating of HDPE,

the abrasive soil environment of the underground ageing test could have, at least partially, exposed some of the BM particles.

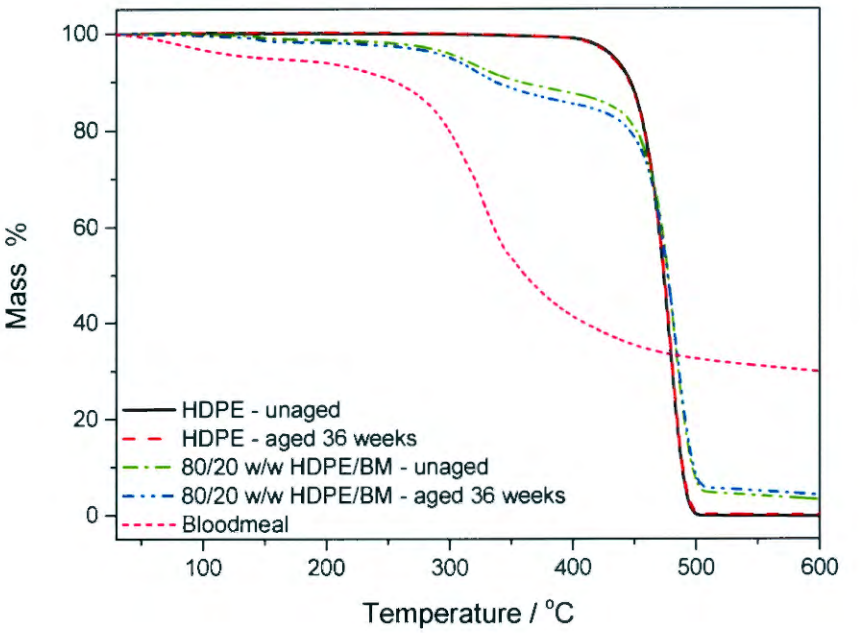


Figure 3.5 TGA curves of unaged bloodmeal, HDPE and the 80/20 w/w HDPE/BM composite films prior to underground ageing and after underground ageing for 36 weeks

Further increase in temperature shows two more degradation steps for the composites. The first degradation step is the degradation of the BM proteins present in the composite, which occurs because the biological BM particles are less thermally stable than the synthetic polyethylene molecules. The second degradation step between 450 and 500 °C is the degradation of polyethylene. It was observed that the addition of BM to HDPE did not affect the thermal stability of HDPE in the composites. If it is taken into account that HDPE represents the largest part of all the composites, it can be seen from Figures 3.4 and 3.5 that there are no major shifts in the curves from approximately 450 °C. This shows that the degradation of HDPE is unaffected by the addition of BM. Based on the char residue of pure BM, the expected char content of the composites was estimated and is shown in Table 3.3, along with the observed char content values. The unaged composites exhibited char residues of approximately 0.6, 0.6, 2.1, and 3.7%. The composite containing 10% BM content showed an average char residue of 2.1% which is very close to the estimated char value for that composition. This result confirms

the BM content of the 10% samples and illustrates that BM was well dispersed in the composite. For the other compositions, the observed char residue varied to some extent from the expected char values. This is probably the result of inefficient distribution of the BM particles in HDPE (evident from the higher standard deviation values). The hydrophilic BM particles probably formed agglomerates in the hydrophobic polyethylene in certain parts of the composite film.

Table 3.3 Average char values for unaged bloodmeal, HDPE, and bloodmeal composites, as well as HDPE and 80/20 w/w HDPE/BM composite aged underground for 36 weeks

Sample	Expected char content / %	Char content from TGA curves / %
Bloodmeal	20	29.4 ± 0.5
HDPE unaged	0	0.2 ± 0.1
HDPE aged 36 weeks	0	0.2 ± 0.0
99/1 w/w HDPE/BM unaged	0.3	0.6 ± 0.8
95/5 w/w HDPE/BM unaged	1.5	0.6 ± 0.1
90/10 w/w HDPE/BM unaged	2.9	2.1 ± 0.4
80/20 w/w HDPE/BM unaged	5.9	3.7 ± 0.6
80/20 w/w HDPE/BM aged 36 weeks	5.9	3.5 ± 0.7

The unaged and aged composite samples followed very similar traces, illustrating that the period of underground ageing had no perceivable effect on the thermal stability of the composite films.

3.1.5 Fourier-transform infrared (FTIR) spectroscopy

FTIR spectra were acquired to verify the presence of certain chemical groups. The existence of certain chemical groups, such as carbonyl compounds, could confirm the occurrence of degradation processes, such as oxidation. Calculation of the carbonyl index is useful to determine the extent of oxidation that has occurred by measuring the intensities of the carbonyl peaks relative to that of the characteristic C-H stretch of the observed spectra [18].

The results of the carbonyl index calculations did not show any observable trends. When amino acids link together to form proteins, a covalent peptide bond forms between the carboxyl group and amine group of two neighbouring amino acids. Thus, there are carbonyl groups present in the peptide bonds of proteins, and in certain side chains of the integral amino acids. The structures of the 20 known amino acids are available in the Appendix. The existence of these carbonyl groups in bloodmeal protein complicated the measurement of the carbonyl index. Additionally, proteins and their secondary structures possess characteristic infrared bands, such as the amide I and amide II bands, respectively observed within the frequency ranges 1600-1690 and 1480-1575 cm^{-1}. The amide I band is designated to C=O stretching, while the amide II band is assigned to CN stretching and NH bending of the peptide bond [19]. Peaks detected in these ranges could also be associated with various carbonyl groups and with the characteristic C-H stretching absorbance which are used for carbonyl index measurements. It can be seen in the tables below that the calculated values for the carbonyl index did not change significantly. It can therefore not be said with certainty that the determined carbonyl index values were an indication of oxidation of the polymer due to ageing, or as a result of chemical groups present in bloodmeal.

When comparing carbonyl index values with ageing time, the following observations were noted. For the thinnest composite films (~0.2 mm), the carbonyl index of the pure HDPE and the 1% composite remained fairly constant as the ageing time increased. The carbonyl index of the 5% composite initially increased slightly, but evened out with ageing time. The 10 and 20% composite carbonyl indices varied marginally to a more significant degree as ageing time increased. Values of the carbonyl index of the ~0.7 mm composite films for all compositions, including pure HDPE, remained within a similar range over the ageing period. The 5, 10 and 20% composites all showed a higher carbonyl index value for the longest ageing time. The thickest composite films (~1.0 mm) displayed similar results, with the exception that the carbonyl index of only the 20% composite increased significantly after 36 weeks of underground ageing. The FTIR spectra of the composites, and graphs of carbonyl index versus ageing time, are available in the Appendix.

It could not be definitively concluded whether the measured carbonyl index was the result of the oxidation of the polymer, due to ageing, or as a consequence of the presence of the bloodmeal proteins in the composites.

Table 3.4 Carbonyl index values calculated for 0.2 mm thick composite films

Ageing time (weeks)	HDPE	99/1 w/w HDPE/BM	95/5 w/w HDPE/BM	90/10 w/w HDPE/BM	80/20 w/w HDPE/BM
0	0.83	0.82	0.82	0.82	0.82
4	0.83	0.82	0.85	0.82	0.86
12	0.83	0.82	0.83	0.86	0.83
20	0.83	0.82	0.83	0.85	0.83
28	0.82	0.83	0.83	0.85	0.82
36	0.82	0.82	0.83	0.83	0.86

Table 3.5 Carbonyl index values calculated for 0.7 mm thick composite films

Ageing time (weeks)	HDPE	99/1 w/w HDPE/BM	95/5 w/w HDPE/BM	90/10 w/w HDPE/BM	80/20 w/w HDPE/BM
0	0.82	0.82	0.82	0.83	0.83
4	0.82	0.82	0.82	0.82	0.83
12	0.82	0.82	0.83	0.83	0.83
20	0.83	0.82	0.82	0.83	0.83
28	0.82	0.82	0.83	0.83	0.82
36	0.82	0.82	0.85	0.84	0.86

Table 3.6 Carbonyl index values calculated for 1.0 mm thick composite films

Ageing time (weeks)	HDPE	99/1 w/w HDPE/BM	95/5 w/w HDPE/BM	90/10 w/w HDPE/BM	80/20 w/w HDPE/BM
0	0.82	0.81	0.82	0.82	0.83
4	0.82	0.82	0.82	0.83	0.85
12	0.83	0.82	0.83	0.83	0.85
20	0.84	0.82	0.82	0.84	0.83
28	0.82	0.82	0.83	0.83	0.82
36	0.82	0.84	0.85	0.83	0.93

3.1.6 Microscopy

3.1.6.1 Optical microscopy

Optical microscopy was used to investigate the morphology of the composites. A 20x magnification was utilized on the 0.2 mm and 1.0 mm composite films to characterise the overall dispersion of bloodmeal in HDPE.

Environmental degradation or deterioration of a polymeric material is defined as any chemical or physical change in a polymer caused by environmental factors such as light, heat, moisture, biological activity or altered chemical condition. Degradation is evident in property changes of the polymer that most often result from modified structural characteristics, such as changes in crystallinity. Changes in the exterior surface, colour or texture can be a simple indication that material properties have been altered. These macroscopic observations can be a useful method to discern possible variations in material properties before more complicated and time-consuming characterisation techniques can be performed [20].

Table 3.7 Optical microscopy images of 0.2 mm thick composite films

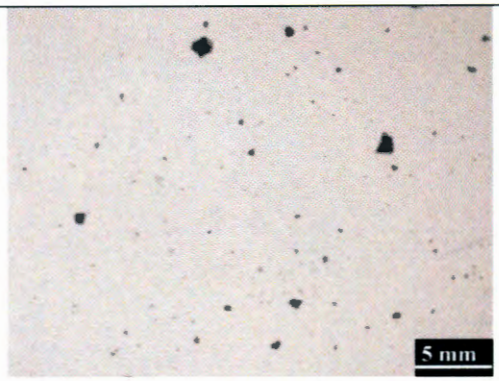
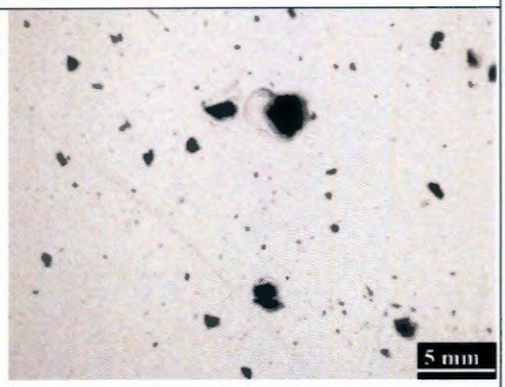
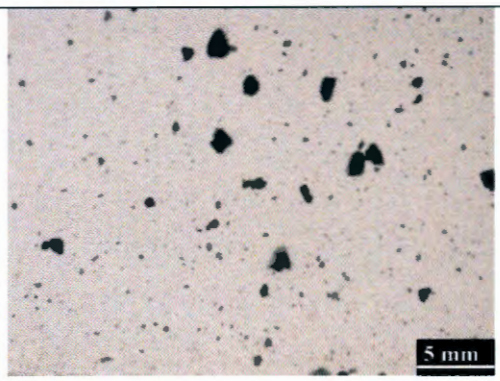
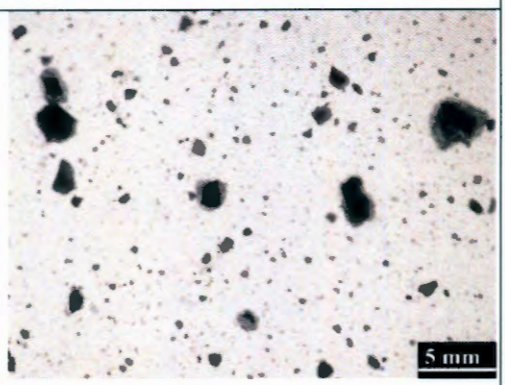
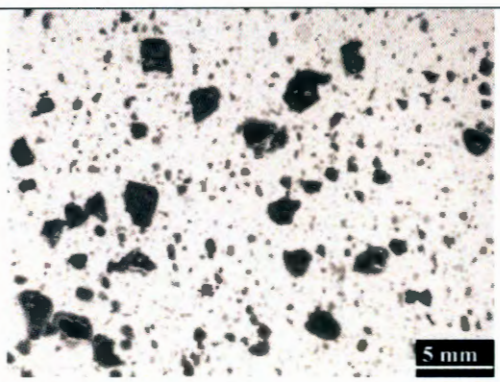
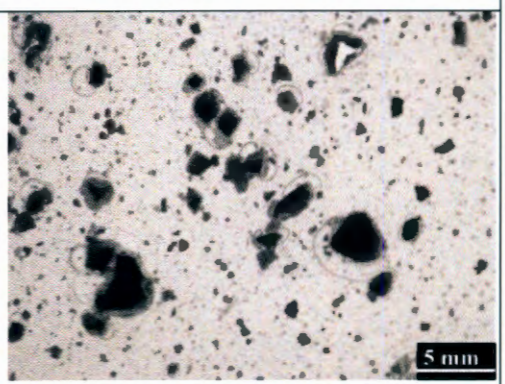
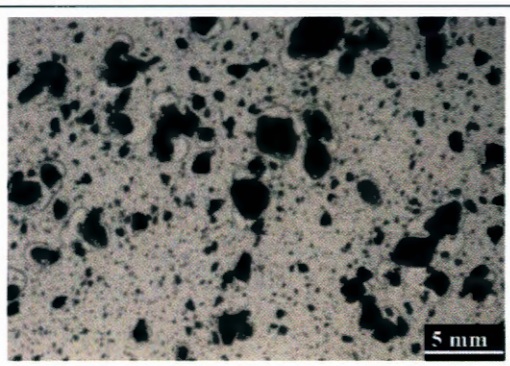
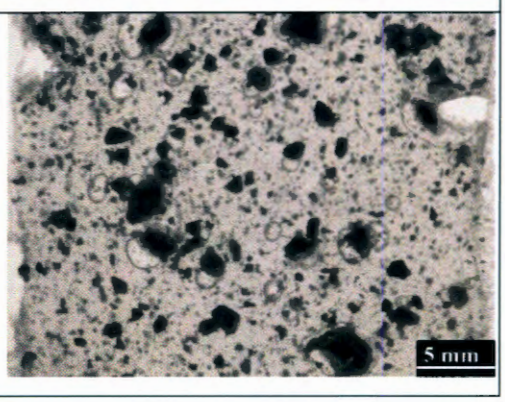
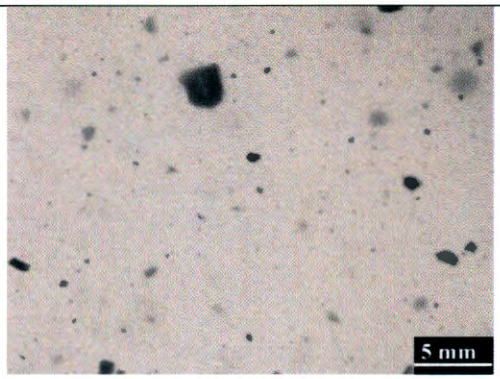
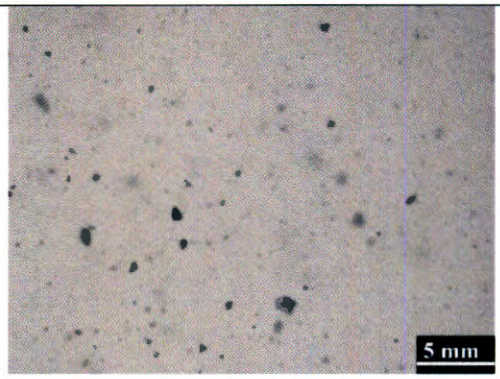
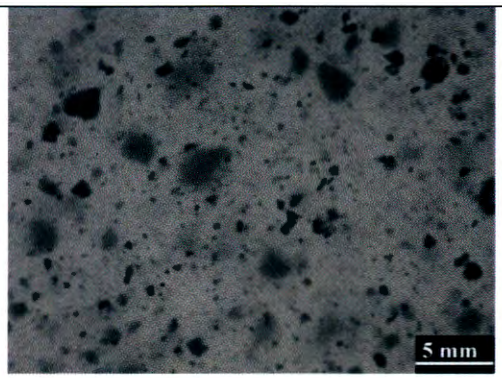
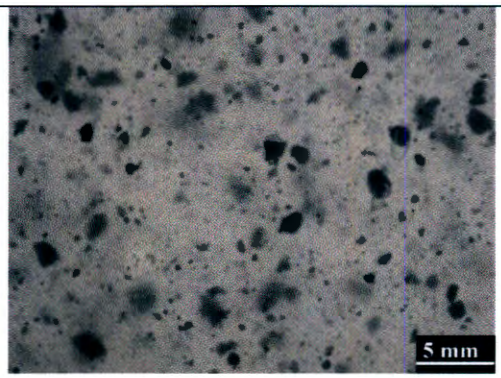
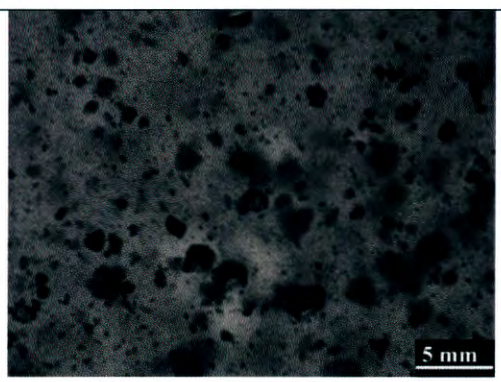
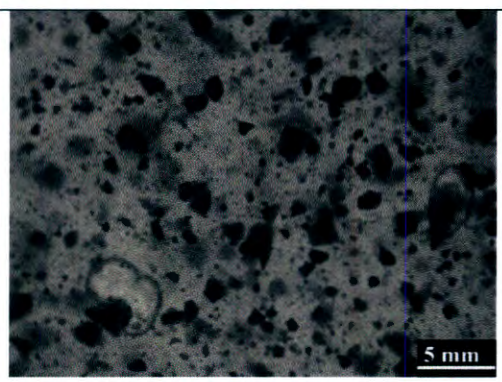
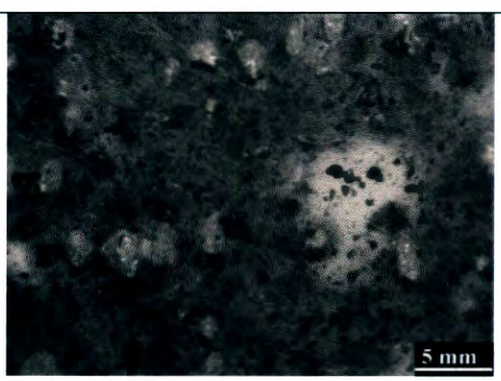
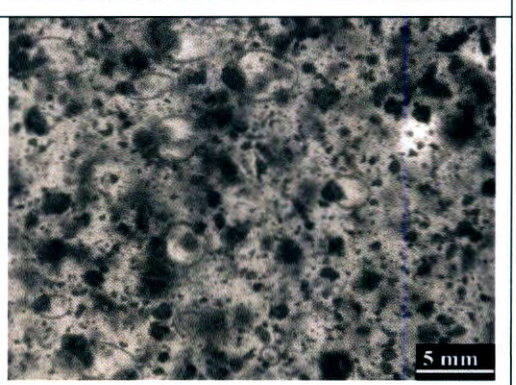
	Unaged samples	Samples aged 36 weeks
99/1 w/w HDPE/BM		
95/5 w/w HDPE/BM		
90/10 w/w HDPE/BM		
80/20 w/w HDPE/BM		

Table 3.8 Optical microscopy pictures of 1.0 mm thick composite films

	Unaged samples	Samples aged 36 weeks
99/1 w/w HDPE/BM		
95/5 w/w HDPE/BM		
90/10 w/w HDPE/BM		
80/20 w/w HDPE/BM		

The BM particles appeared to be fairly evenly dispersed throughout the HDPE matrix (Tables 3.6 and 3.7). The expected noticeable effects of ageing and degradation, for example, discolouration, or the development of cracks in the polymer surface, were not observed in the aged films. Bubbles were seen in some of the films of both thicknesses, and for both the unaged and aged samples. This could have resulted due to air trapped in the polymer, or around the BM particles, during mixing or melt pressing. The presence of bubbles are also an indication that the adhesion between the HDPE and the BM particles was imperfect. The presence of bubbles in the composite films can compromise the structural integrity of the material and can negatively impact mechanical properties. In general, it was observed that the presence of BM did not improve the mechanical properties of the composites due to imperfect adhesion between the HDPE matrix and the BM particles. The occurrence of bubbles very possibly contributed to the negative effects of BM on the mechanical properties. Addition of compatibilising agents could aid the mixing process, making sure the components have better adhesion [21,22].

Holes were seen in the 0.2 mm thick aged films, but not in the 1.0 mm films. Since the adhesion between the BM particles and the HDPE was not ideal, it is possible that a BM particle could have become dislodged from the thin HDPE matrix in the abrasive soil environment, during underground ageing, or during handling. In the thicker films, the BM particles had greater coverage by the polymer and would not have been as easily removed.

3.1.6.2 Scanning electron microscopy (SEM)

Images of the unaged and aged samples of HDPE and the 80/20 w/w HDPE/BM composites were obtained using SEM. It was observed that the surface of the HDPE samples looked very similar before and after underground ageing (Figure 3.6a and 3.6b). Since it is well known that polyethylene is resistant to degradation, it was expected that the material would not exhibit any changes due to underground ageing.

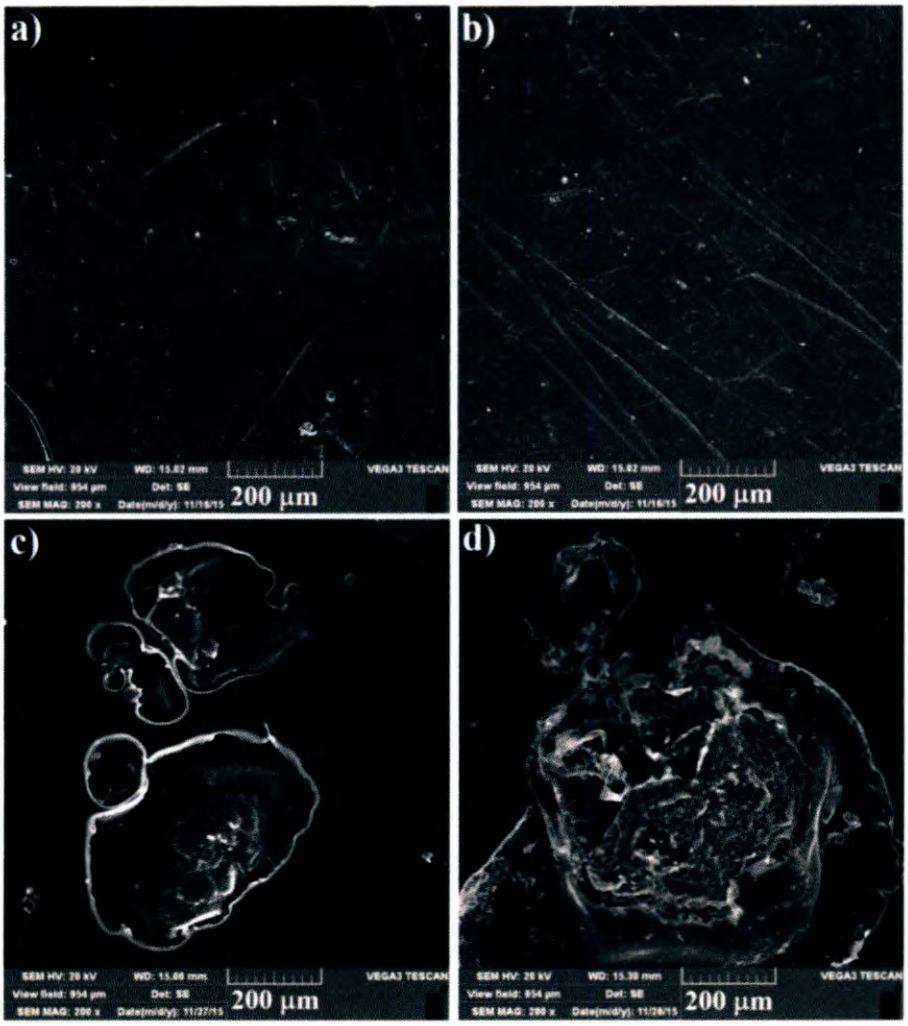


Figure 3.6 SEM images of a) unaged HDPE, b) HDPE aged underground for 36 weeks, c) unaged 80/20 w/w HDPE/BM, and d) 80/20 w/w HDPE/BM aged underground for 36 weeks.

In Figure 3.6, the images of the unaged and aged 80/20 w/w HDPE/BM composites are shown as (c) and (d), respectively. The surface of the particles of the unaged samples appeared smooth, it seems that the particles are covered by a thin layer of HDPE. It was clearly seen that the particle surface in the aged samples was coarse and irregular, as if the surrounding HDPE had been 'eaten away' or degraded. This irregular surface was observed for the whole sample of 80/20 w/w HDPE/BM composites that was investigated after ageing for thirty-six weeks. A possible explanation for this observation is that the presence of BM in the HDPE film, in the underground soil conditions, caused some degradation of the HDPE.

3.1.8 Tensile testing

Tensile tests of unaged samples were performed to show the initial effects of the addition of bloodmeal on the mechanical properties of HDPE. The mechanical properties of the aged samples were investigated to evaluate the influence of the bloodmeal in HDPE over time. The yield stress and elongation at break values were read off the stress-strain curves for all the composites. Young's modulus, or elastic modulus, was calculated from the initial part of the stress-strain curve (within 1.8% strain) for all film thicknesses of each ageing time.

The structure of the crystalline regions in a polymeric material, e.g. amount of crystallites, crystallite sizes, etc., play an important role in the mechanical properties of a material. The degree of crystallinity directly affects the strength of a material, and its ductility. In this study, three films of differing thicknesses where prepared for each composition, 0.2, 0.7, and 1.0 mm. During the preparation of the composite films, the degree of crystallinity slightly increased as the thickness of the films increased since the thicker films could cool from the melt somewhat slower than the thinner films. The influence of pre-cooling is evident in the comparison of the properties exhibited by the films of different thicknesses. This effect is also supported by the melting enthalpy results obtained by the DSC analyses in this study, i.e. ΔH_m^{norm}(HDPE) = 182.4 J.g^{-1} for the 0.2 mm film, and ΔH_m^{norm}(HDPE) = 198.3 J.g^{-1}. The results table can be found in Table A.3.2 in the Appendix.

The samples were prepared using a cooling rate that corresponds with that used during industrial production conditions. HDPE prepared in this way tends to crystallize over time, a process known as physical ageing, or structural recovery [23,24]. This crystallization can be accelerated by using additional thermal treatment before ageing, such as heat treatment in an oven or radiation with UV light. In many similar experiments, authors performed thermal treatments of the samples before performing an ageing experiment to stabilise the samples and produce a uniform thermal history [25–27]. This strategy was not implemented in this study, because the intention of this work was to investigate the effect of film thickness and also the ageing behaviour of samples prepared in 'real' industrial conditions.

Young's modulus versus weight percentage BM of the unaged samples for all the compositions are presented in Figure 3.7. The composite sample containing 1% BM showed higher modulus

values than HDPE. This could be the result of the higher crystallinity of the sample, as can be seen from the DSC results (Table 3.2). After the initial increase, the modulus of the samples decreased with increasing concentration of BM, for all the film thicknesses. Considering that the normalised melting enthalpies, i.e. the degree of crystallinity, of the 10 and 20% samples are similar to that of HDPE, it can be concluded that the decrease in modulus with an increasing concentration of BM is probably due to a softening effect of the organic filler in the composite. The results also show that the effect of thickness is not very pronounced. Samples with a thickness of 0.2 mm show somewhat lower values of modulus, which can be explained by lower crystallinity values compared to the thicker film samples.

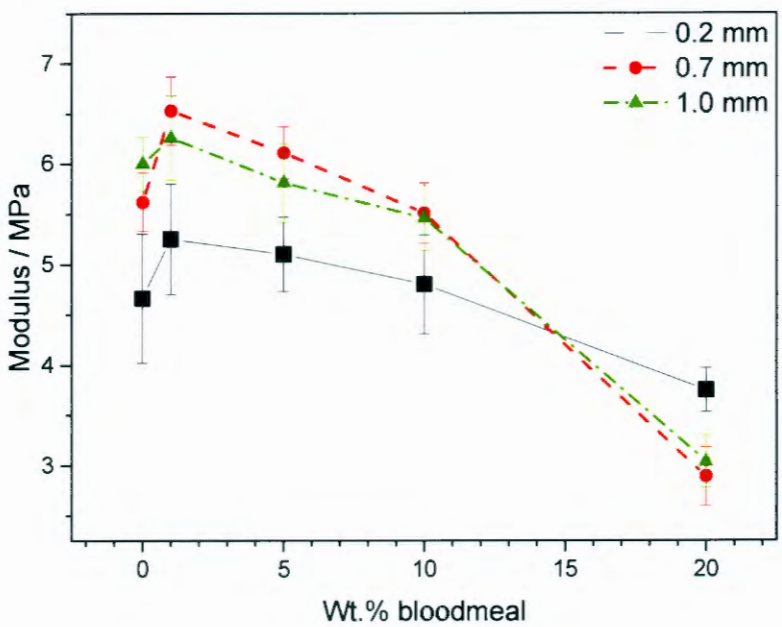


Figure 3.7 Young's modulus values for unaged composite films with different thicknesses

Figure 3.8 shows the average elongation at break values for the unaged composites for all three thicknesses. As the BM content of the composite was increased, the elongation at break values decreased, with the larges decrease observed for the lowest BM content. The elongation at break for HDPE was significantly higher than that of the composites, which was expected since polyethylene in generally known for its good mechanical properties. The elongation at break values of the composites decreased with BM loading due to the imperfect adhesion between HDPE and BM, and the BM particles acting as stress concentration points, because of their respective hydrophobic and hydrophilic natures. For HDPE, the elongation at break increased

as the film thickness increased because the thicker film contained a slightly higher degree of crystallinity due to the effect of pre-cooling. This was also observed for the 1 and 5% composites, but not for the 10 and 20% composites, possibly because the likelihood of agglomeration of BM particles increased as the BM content increased. The changes in elongation at break with increasing BM concentration are conspicuous, which leads to the inference that the inclusion of BM in HDPE considerably affects the amorphous phase of HDPE. Since the elongation at break is mostly dependent on the viscosity of the amorphous phase at the temperature of testing, decreased elongation at break values indicate an influence of the addition of BM to the amorphous phase of the polymer [28–30]. These changes in the amorphous phase of HDPE had no effect on the crystalline phase, since the melting temperature of the composites containing BM were relatively similar to the melting temperature of HDPE, as seen in Table 3.2.

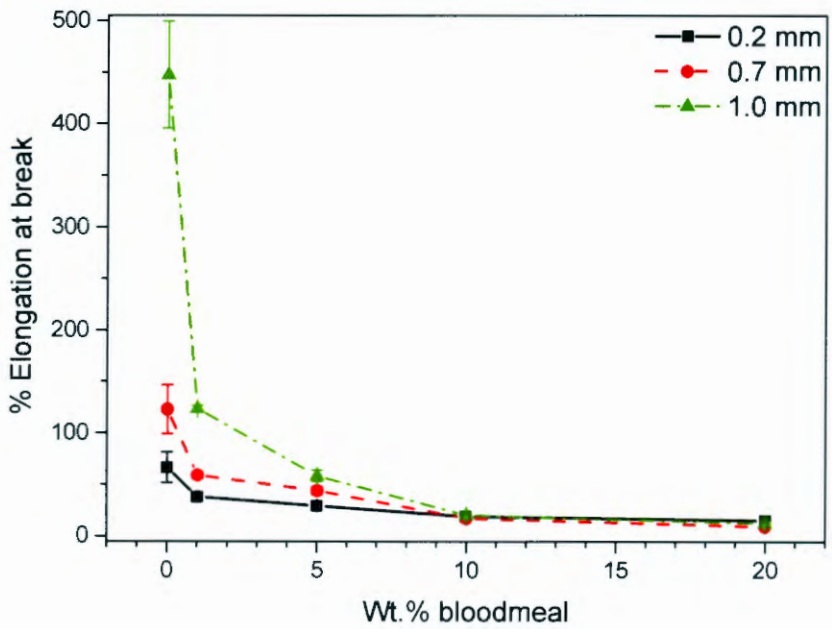


Figure 3.8 Elongation at break values for unaged composite films with different thicknesses

Before the yield point of a material, if a force exerted, the material will deform elastically and can return to its original shape when the applied force is removed. After the yield point, the material is irreversibly deformed. The stress at yield can be explained as the stress at which a material begins to deform plastically and will not return to its original shape if the applied force

is removed [31]. Similar to the results for Young's modulus (Figure 3.7), the initial addition of BM showed an increase in the yield stress, compared to HDPE. Further increase in BM content exhibited lower yield stresses. This was due to the poor adhesion that was observed between the BM particles and the PE matrix, as was also evident in the other mechanical properties. It was expected that the stress at yield would increase with the thickness of the films. This result was observed to some extent for all the composite compositions.

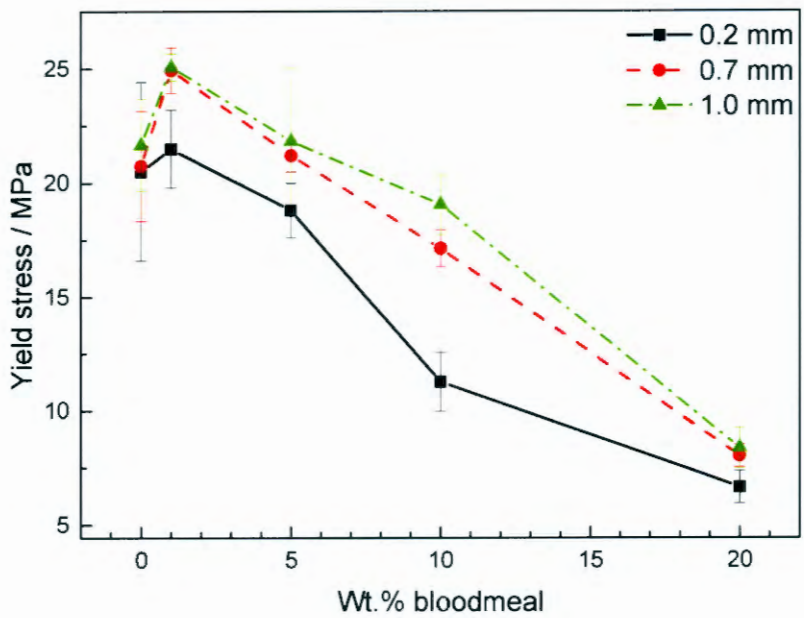


Figure 3.9 Yield stress values for unaged composite films with different thicknesses

Figures 3.9 to 3.11 illustrate the effect of underground ageing on Young's modulus of the composite films of different thicknesses. During the first four weeks' ageing time, for all the film thicknesses, Young's modulus increased by about 200% for all the compositions of the composite films. This observation is a consequence of the process of natural stabilisation or crystallization of the material with time, also known as physical ageing, or structural recovery [23,24]. For all the film thicknesses, Young's modulus only slightly fluctuated with an increase in underground ageing time. The changes in modulus were more pronounced in the 0.2 mm composite films and became less pronounced as the film thickness increased. It was also noted that the modulus generally decreased with increasing BM load.

The modulus values remained fairly constant after the first ageing time for neat HDPE (Figure 3.9). This was a predictable outcome since it was not anticipated that the underground ageing

treatment would have a significant effect on synthetic polymer films. Young's modulus showed a moderate increase for the 1% BM composite from four to twenty weeks of ageing in soil. Although, after 20 weeks, the modulus decreased. As the ageing time increased for the 5, 10, and 20% BM samples, the modulus decreased to varying extents. It can be seen in Figure 3.9 that the decrease in modulus corresponds with the BM content of the films. Composites with higher BM content contained more BM particles, and therefore there is a higher possibly of the occurrence of agglomeration. The DSC results showed a decrease in crystallinity, and the BM particles probably do not have a high enough inherent stiffness to compensate for the loss of stiffness brought about by the lower crystallinity. Since the adhesion between the BM and HDPE was not ideal, it is plausible that some of the BM particles could have become dislodged from the HDPE matrix with time, leaving small "holes" in the film. The consequence would be most pronounced for the 0.2 mm thick composite films. This "perforated area" in the film would compromise the structural integrity of the film, reducing the strength of the material.

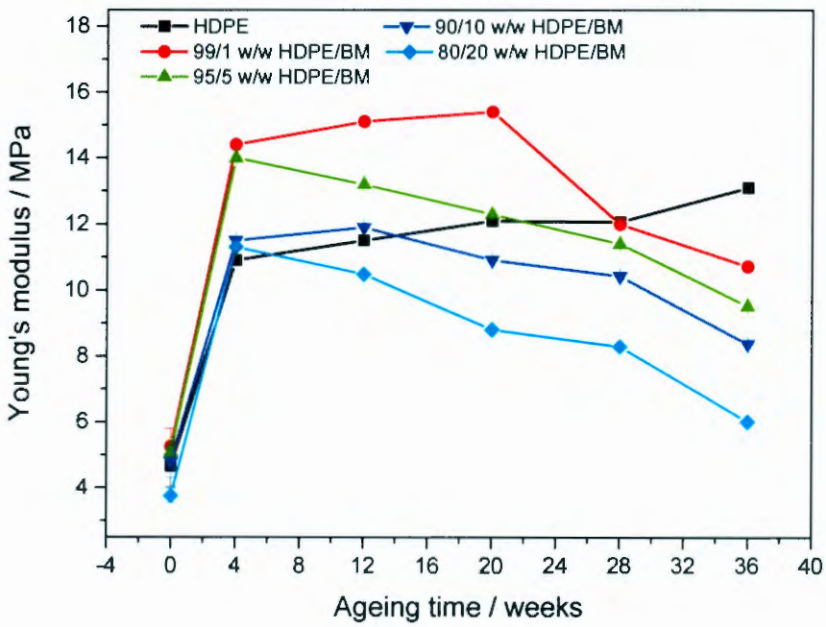


Figure 3.10 Young's modulus for all the 0.2 mm thick composite films as function of ageing time

Figure 3.10 and 3.11 show that, for the 0.7 and 1.0 mm HDPE films, the values for Young's modulus show only minor fluctuations with increasing underground ageing time. In contrast to the results for the 0.2 mm thick film of 1% BM, the modulus values for the 0.7 and 1.0 mm films followed a similar trend to that of HDPE for the same film thicknesses. As explained

earlier, the effect of pre-cooling could have occurred in the thicker films with low BM content, resulting in slightly more crystalline material that possesses a higher modulus. Higher contents of BM also only displayed minor fluctuations as the ageing time increased for both 0.7 and 1.0 mm film thicknesses. The influence of ageing was marginally more prominent for the 0.7 mm thick films than for the 1.0 mm thick films, also as a consequence of the effect of pre-cooling of the thicker composite films.

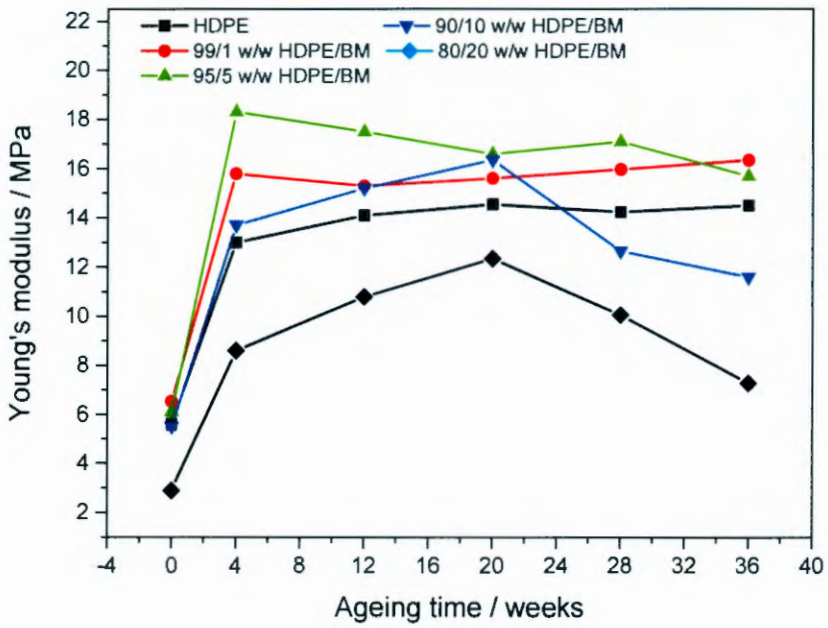


Figure 3.11 Young's modulus for all the 0.7 mm thick composite films as function of ageing time

A summary of the behaviour of Young's modulus as a function of underground ageing time is presented in Figure 3.12 for all the film thicknesses. It presents a comparison of the modulus values between 4 and 36 weeks of underground ageing. In order to exclude from the ageing behaviour of the composites the effects of crystallization that occur due to physical ageing, the modulus of the unaged samples during the first four weeks were omitted.

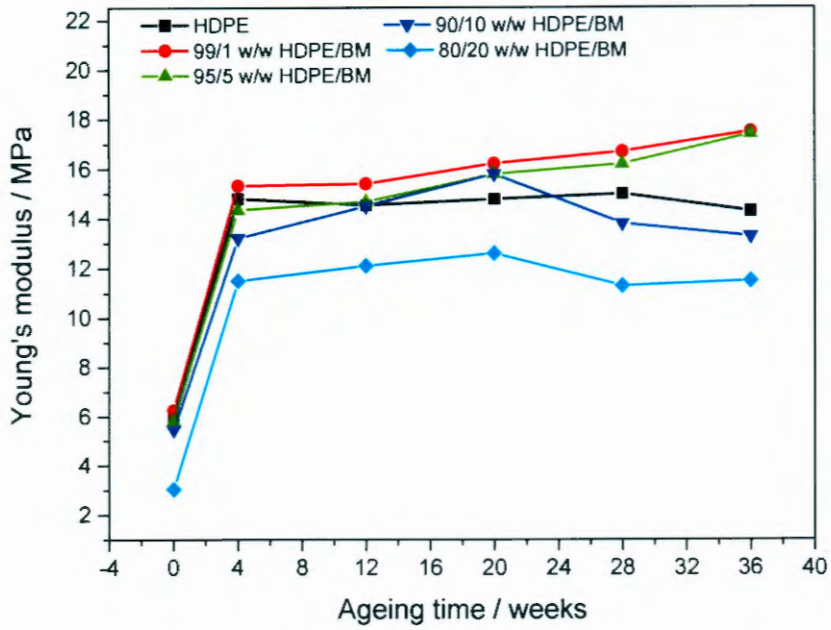


Figure 3.12 Young's modulus for all the 1.0 mm thick composite films as function of ageing time

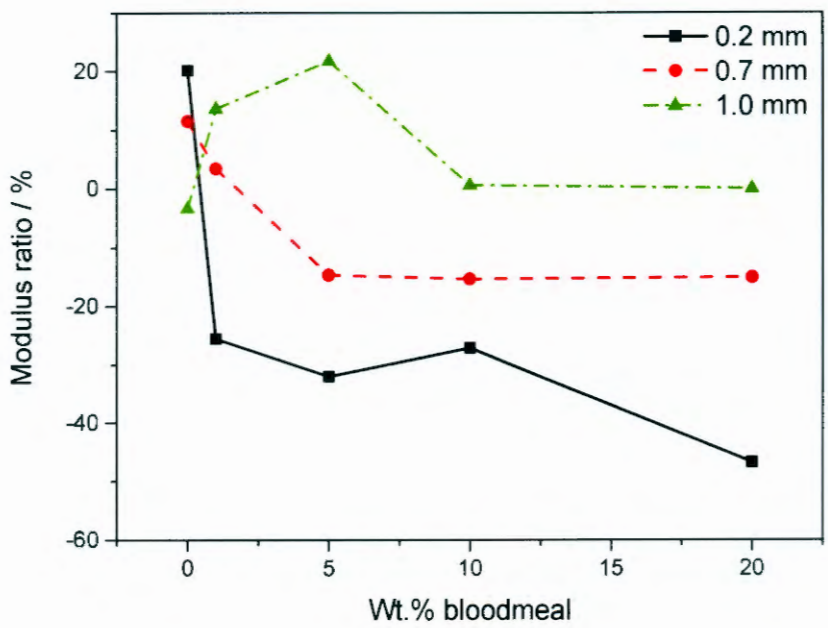


Figure 3.13 Percent change in modulus between tbe fourth and thirty-sixth week of ageing

The changes presented are calculated according to Equation 3.1.

$$\Delta E_{36-4}(\%) = 100 \cdot \frac{E_{36}-E_4}{E_4} \qquad (3.1)$$

where E_{36} is the average modulus after thirty six weeks of underground ageing (final ageing time) and E_4 is the average modulus after four weeks of underground ageing (first ageing time).

The representation indicates that the effect of underground ageing is more pronounced in the 0.2 mm thick composite films. This is a reasonable conclusion since the thinner films, having a reduced cross-sectional area, possess a higher sensitivity to the progress of ageing effects from the film surface to the sub-surface of the film.

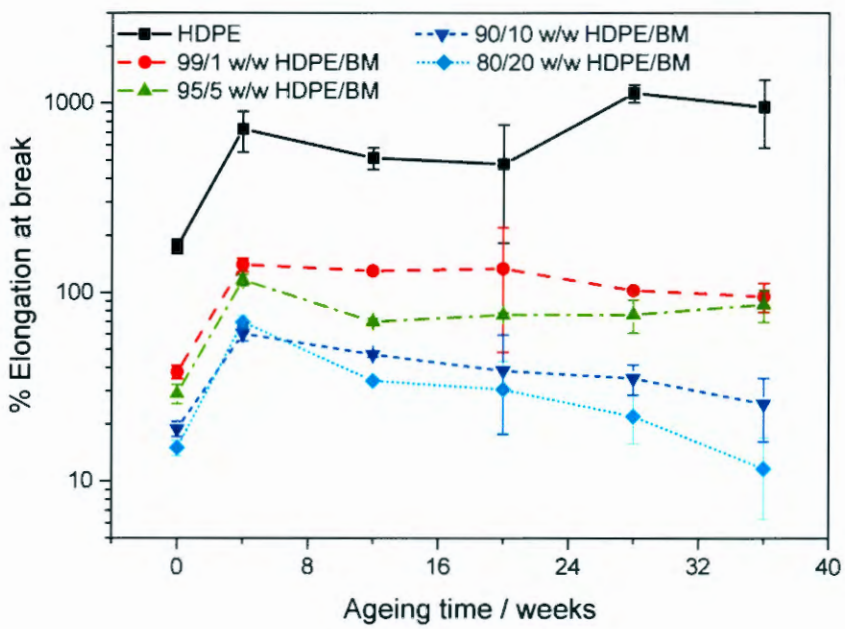


Figure 3.14 Elongation at break values versus ageing time for 0.2 mm thick composites

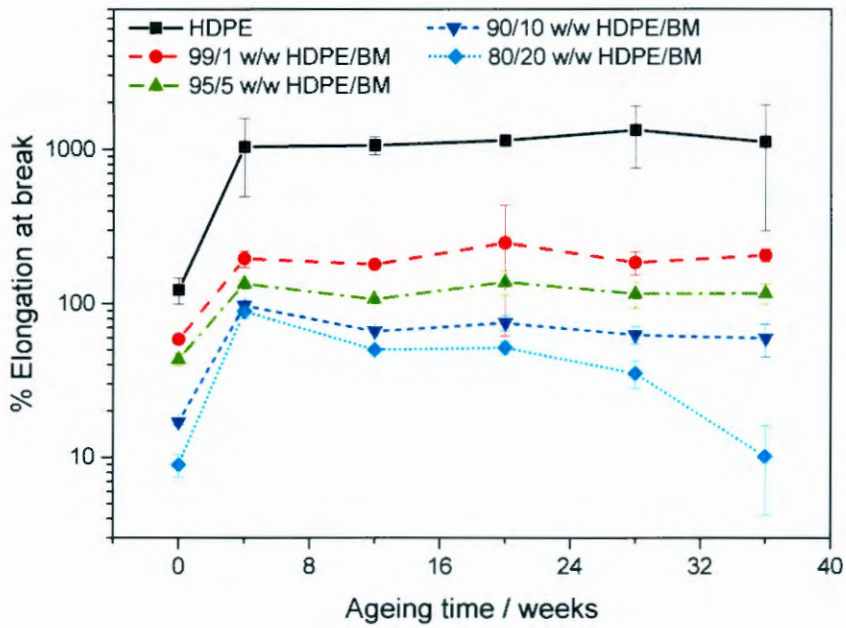


Figure 3.15 Elongation at break values versus ageing time for 0.7 mm thick composites

Figures 3.13, 3.14, and 3.15 present the effect of ageing on the elongation at break for the samples with different thicknesses. For all the film thicknesses, the HDPE again showed significantly higher values than the composites. Generally, the elongation at break values decreased with an increase in BM content, which is a consequence of the poor adhesion between the hydrophobic HDPE matrix and the hydrophilic BM particles. The elongation at break of all the samples, for each composition and all film thicknesses exhibited a noteworthy increase during the first four weeks of ageing, again due to the pre-cooling effect of the samples. The values remained relatively constant, for all the film thicknesses, but the 20% BM composite films displayed the most observable deviations with prolonged ageing time.

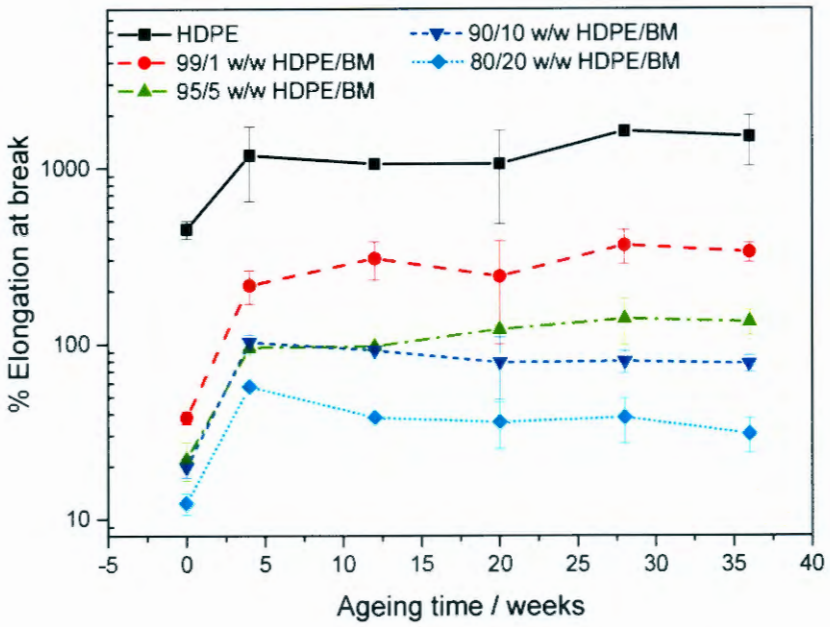


Figure 3.16 Elongation at break values versus ageing time for 1.0 mm thick composites

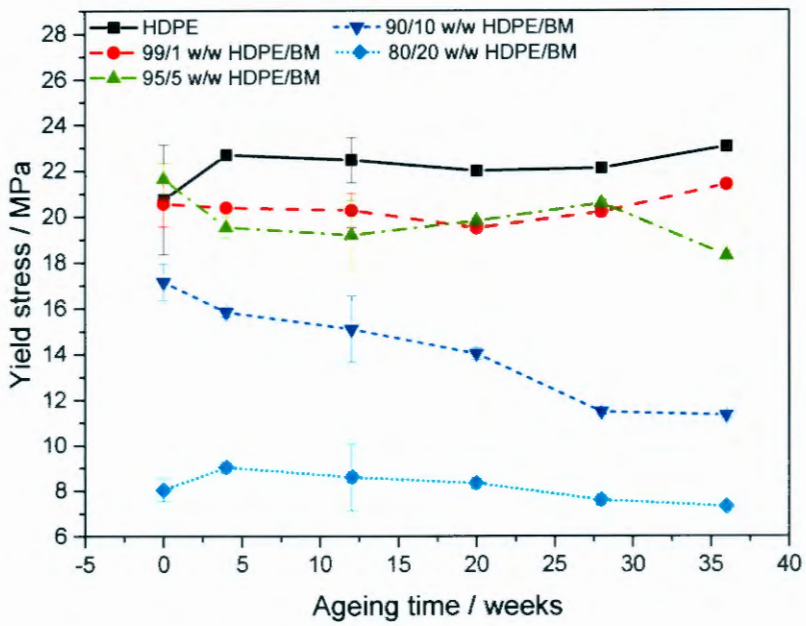


Figure 3.17 Stress at yield values versus ageing time for 0.7 mm thick composites

The effects of underground ageing on the stress at yield were observed to be similar for the samples with different thicknesses. For this reason, only the effects of ageing on the yield stress of the 0.7 mm thick samples is presented in Figure 3.16. The influence of pre-cooling on the

yield stress was not as clearly observed for all compositions of the 0.7 mm thick films. The HDPE values were only slightly higher than those of the composites, with the yield stress for the 1 and 5% samples being comparatively similar to those of HDPE over time. The 10% BM samples presented a well-defined decrease in yield stress with increasing ageing time. For the 20% BM samples, the yield stress was considerably lower than those of the other composites, but consistent with HDPE, and the 1 and 5% composites, the values remained relatively constant over time. The yield point of a material is the point at which elastic deformation can no longer occur. Thus, the stress at yield can be thought of as the minimum stress at which permanent strain materialises [32]. Since the observed values for the stress at yield did not display any significant changes with ageing time, it can be said that the stress at yield characteristics of the material were not noticeably altered due to underground ageing. The yield stress clearly decreased as the weight percentage of bloodmeal increased due to poor adhesion between the HDPE matrix and the BM particles.

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Chapter 4

Conclusions

This work aimed to prepare HDPE composites with bloodmeal, in an endeavour to create a degradable material with similar properties to neat HDPE. The main objective was to alleviate the increasing amount of environmental pollution caused by non-degradable synthetic wastes. Both unaged and aged composites were characterised with thermal methods, the mechanical properties were studied, and the morphology was investigated with ATR-FTIR spectroscopy, optical microscopy and SEM.

The two microscopy techniques were used to assess the distribution of BM in the HDPE matrix, and attempt to identify any ageing effects on the film surfaces resulting from underground ageing. The optical microscopy pictures showed that the BM was relatively well dispersed in HDPE. No obvious signs of ageing such as cracking, discolouration or yellowing, was observed with optical microscopy. The SEM images of the surface of the 80/20 w/w HDPE/BM sample, subjected to underground ageing for thirty-six weeks, appeared as if the HDPE around the BM particles had been "eaten away" or degraded. From the images it could be concluded that degradation of the HDPE film surface could have occurred due to underground ageing processes.

It was seen that the period of underground ageing exhibited a more pronounced effect on the mechanical properties of the thinnest composite films (0.2 mm), compared to those of the thicker composite films. This was expected since the BM particles were situated on or near the surface of the films and the thinnest films possessed a smaller cross-sectional area, making the films more susceptible or receptive to the effects of ageing.

It was established that the addition of BM to HDPE does increase the moisture content of the composite to a certain degree. The moisture content of the composites was expected to increase with the addition of BM, and this was only partially observed because of the encapsulating influence of HDPE. The ability of the material to absorb water was marginally improved with the addition of BM, as seen in the results of the water absorption experiments. Increased

moisture retained within the composite could promote hydrolytic degradation of the material, but this aspect was not investigated in this study. Thus, the addition of bloodmeal could affect the accepted mechanism of the degradation of polyethylene to include hydrolytic degradation.

The inclusion of BM increased the modulus of the unaged composites due to the reinforcing effect of the filler, but this improvement was only observed for the 1% BM composite. Generally, there was a decrease in the modulus, stress at yield, and elongation at break of the unaged composites. The adhesion between the BM particles and the HDPE matrix appeared to be fairly poor, which negatively affected the mechanical properties. The duration of underground ageing did not significantly affect the mechanical properties of the composites since the average values did not fluctuate to a large extent.

As a general conclusion, it was found that the inclusion of bloodmeal in HDPE did not have an obviously positive or negative influence on the properties or environmental degradation of the resulting composites. Underground ageing of up to 36 weeks had little effect on the properties of the material, compared to the unaged material. No unambiguous claims can therefore be made about the effect of the addition of BM on the degradation characteristics of HDPE derived from the characterisations performed in this study. It is suggested that the underground ageing period be extended to at least 52 weeks, and that UV-initiated degradation in the open air also be investigated. This can be complemented by artificial ageing in a weatherometer. Another possibility is the improvement of the interaction between the BM particles and the HDPE matrix in order to reduce the negative influence of BM on the mechanical properties of HDPE, and to possibly contribute to more effective environmental degradation.

Acknowledgements

"I can do all things through Christ who strengthens me" Philippians 4:13

Firstly, I would like to thank my supervisor, Prof. A.S. Luyt for his support and guidance throughout my research project. Prof. Luyt always led by example, and I learnt a great deal from him. I would also like to express my gratitude to Dr. D. Dudić who was a constant source of assistance with his famous "step by step" statements of encouragement. Thank you gentlemen, without the benefit of your assistance, I would not have achieved this milestone.

I would like to thank the University of the Free State (UFS) for financial support and allowing this opportunity to further my studies and pursue my goals.

I am also grateful to all my friends and colleagues in the Polymer Research Group of UFS (Qwaqwa Campus), always ready with words of encouragement and advice. Special thanks to Dr. Puseletso Mofokeng and Ms. Motshabi Sibeko, whose friendship and inspiration is a reliable constant.

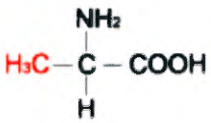
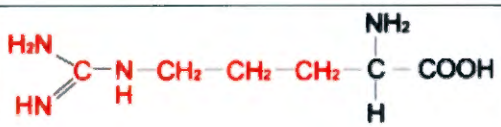
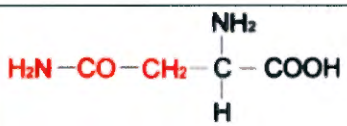
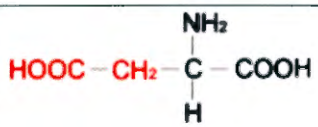
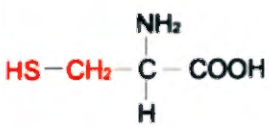
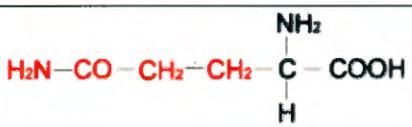
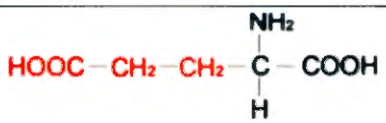
To Mrs. Marlize Jackson, the Faculty secretary, thank you for all the help and friendship you provided throughout the duration of my studies. Your contribution to our Faculty is invaluable.

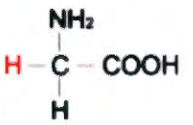
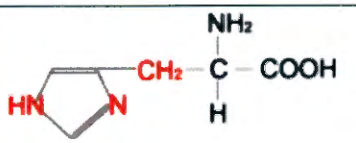
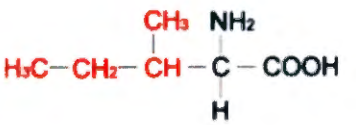
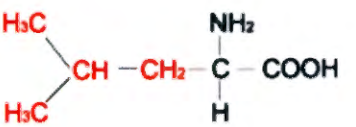
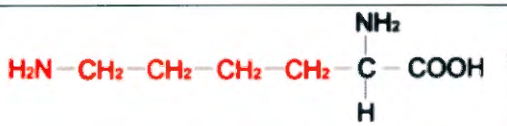
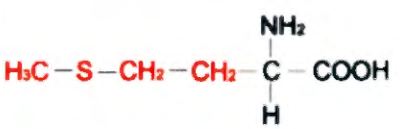
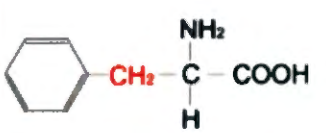
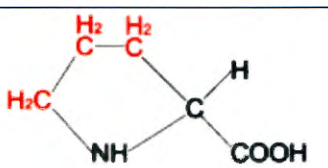
Many thanks to the König and De Wet families for the constant love and support.

Finally, I would like to thank everyone who has supported me academically and emotionally during this time, especially my friends and family, may God bless you all!

Appendix

Table A.1.1 Structures of amino acids [1]

AMINO ACID	STRUCTURE	PROPERTIES OF SIDE CHAIN
Alanine		Non-polar / hydrophobic Uncharged Aliphatic
Arginine		Hydrophilic Alkaline, positively charged
Asparagine		Polar / hydrophilic Uncharged
Aspartate / Aspartic acid		Hydrophilic Acidic, negatively charged
Cysteine		Polar / hydrophilic Uncharged Sulphur-containing
Glutamine		Polar / hydrophilic Uncharged
Glutamate / Glutamic acid		Hydrophilic Acidic, negatively charged

Glycine		Non-polar Uncharged Aliphatic
Histidine		Hydrophilic Alkaline, positively charged
Isoleucine		Non-polar / hydrophobic Uncharged Aliphatic
Leucine		Non-polar / hydrophobic Uncharged Aliphatic
Lycine		Amphipathic Alkaline, positively charged
Methionine		Polar / amphipathic Uncharged Sulphur-containing
Phenylalanine		Non-polar / hydrophobic Uncharged Aromatic
Proline		Non-polar / hydrophobic Uncharged

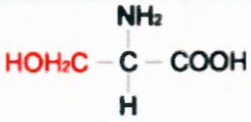
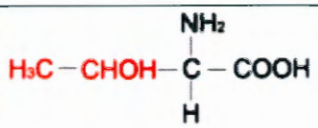
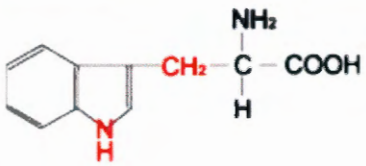
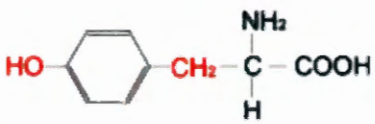
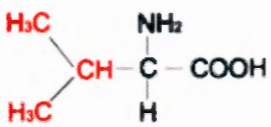
		Aliphatic
Serine		Polar / hydrophilic Uncharged
Threonine		Polar Uncharged
Tryptophan		Non-polar / amphipathic Uncharged Aromatic
Tyrosine		Polar / amphipathic Uncharged Aromatic
Valine		Non-polar / hydrophobic Uncharged Aliphatic

Table A.1.2 Amino acid content of bloodmeal [2]

AMINO ACID	CONTENT / %
Alanine	7.73 ± 0.09
Apartic acid	10.51 ± 0.09
Arginine	4.14 ± 0.06
Cystine	0.99 ± 0.002
Glutamic acid	8.74 ± 0.10
Glycine	4.29 ± 0.08
Histidine	6.05 ± 0.30
Isoleucine	0.93 ± 0.03
Leucine	12.55 ± 0.10
Lysine	9.46 ± 0.19
Methionine	0.70 ± 0.03
Phenylalanine	6.78 ± 0.10
Proline	3.72 ± 0.09
Serine	3.97 ± 0.10
Threonine	3.89 ± 0.14
Tyrosine	2.49 ± 0.06
Valine	8.84 ± 0.11

Table A.3.1 Moisture content for pure bloodmeal powder

Initial BM mass / g	After drying / g	Difference / g	Moisture / %	Average / %
1.0188	0.9619	0.0569	5.6	5.0 ± 0.7
1.0122	0.96	0.0522	5.2	
1.0100	0.9668	0.0432	4.3	

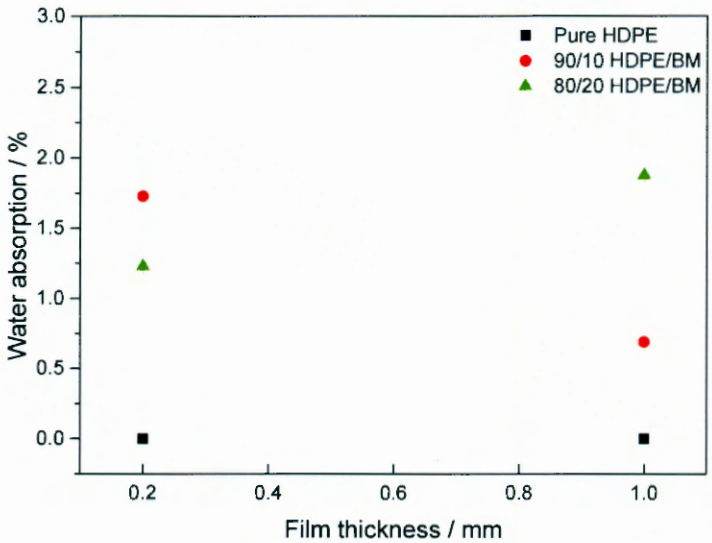
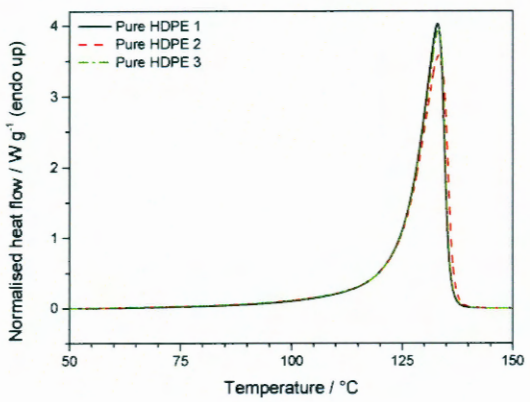
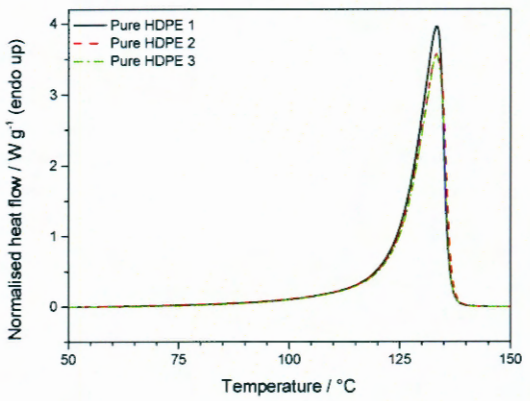
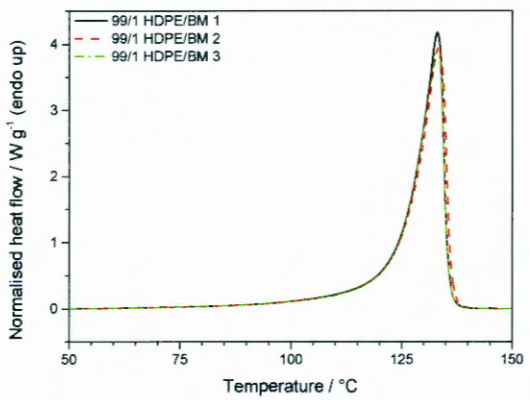
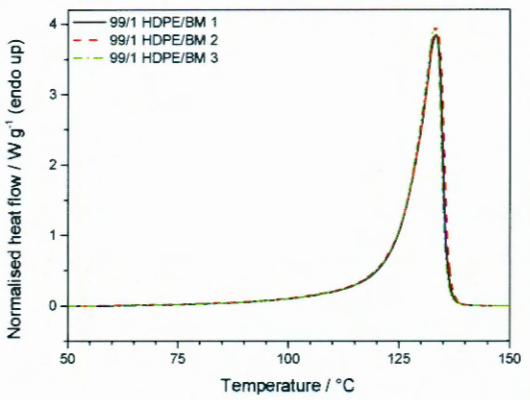


Figure A.3.1 Comparison of water absorption values for pure HDPE, as well as 90/10 w/w and 80/20 w/w HDPE/BM composite films prior to underground ageing

Table A.3.2 Table of DSC results for unaged HDPE films of different thicknesses

HEATING				
Sample		T_m / °C	ΔH_m / J g^{-1}	ΔH_m^{norm} / J g^{-1}
Unaged Pure HDPE	0.2 mm	130.1 ± 0.4	182.4 ± 3.6	182.4 ± 3.6
	0.7 mm	133.1 ± 0.3	196.2 ± 2.8	196.2 ± 2.8
	1.0 mm	133.2 ± 0.3	198.3 ± 4.1	198.3 ± 4.1
COOLING				
Sample		T_c / °C	ΔH_c / J g^{-1}	ΔH_c^{norm} / J g^{-1}
Unaged Pure HDPE	0.2 mm	114.9 ± 0.5	-176.3 ± 10.4	-176.3 ± 10.4
	0.7 mm	117.5 ± 0.2	-189.7 ± 8.3	-189.7 ± 8.3
	1.0 mm	117.6 ± 0.4	-191.7 ± 9.2	-191.7 ± 9.2

Table A.3.3 Table of DSC heating curves for all composites, unaged and composites aged for 36 weeks

<table>
<tr><th colspan="2">SECOND HEATING</th></tr>
<tr><td>HDPE – unaged</td><td>HDPE – aged 36 weeks</td></tr>
<tr><td> 
</td><td> 
</td></tr>
<tr><td>99/1 w/w HDPE/BM – unaged</td><td>99/1 w/w HDPE/BM – aged 36 weeks</td></tr>
<tr><td> 
</td><td> 
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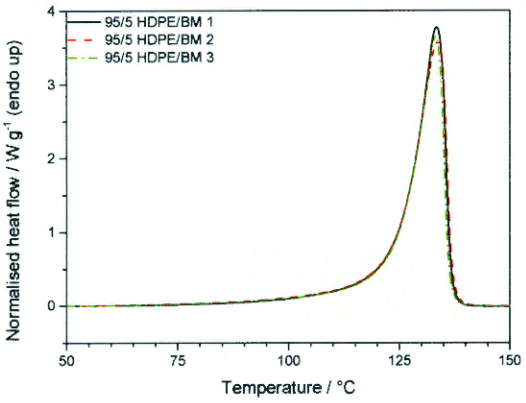
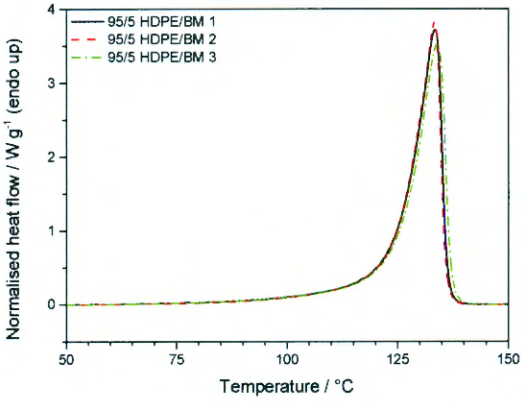
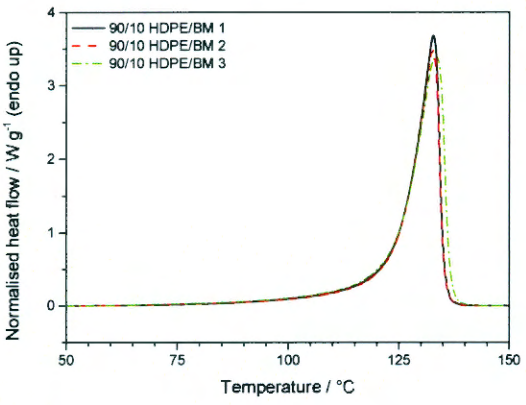
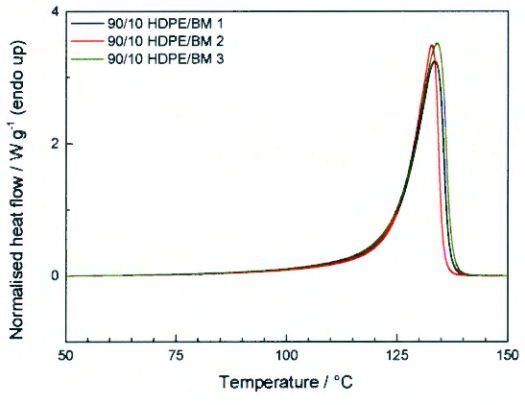
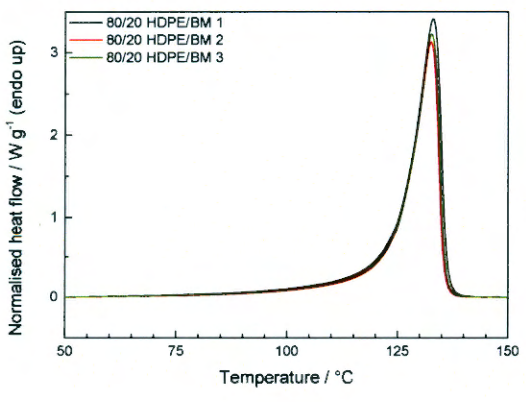
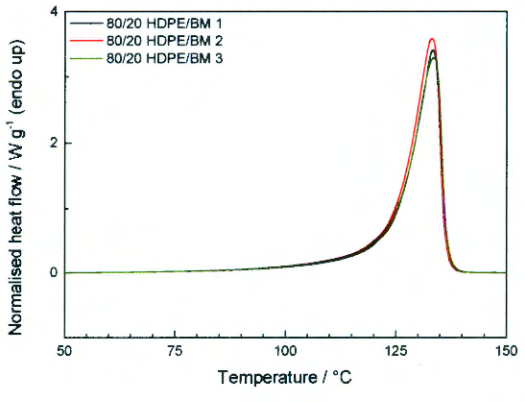
95/5 w/w HDPE/BM – unaged	95/5 w/w HDPE/BM – aged 36 weeks
	
90/10 w/w HDPE/BM – unaged	90/10 w/w HDPE/BM – aged 36 weeks
	
80/20 w/w HDPE/BM – unaged	80/20 w/w HDPE/BM – aged 36 weeks
	

Table A.3.3 Table of DSC cooling curves for all composites, unaged and composites aged for 36 weeks

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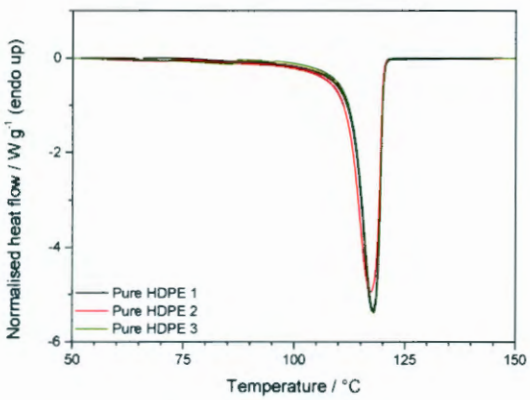
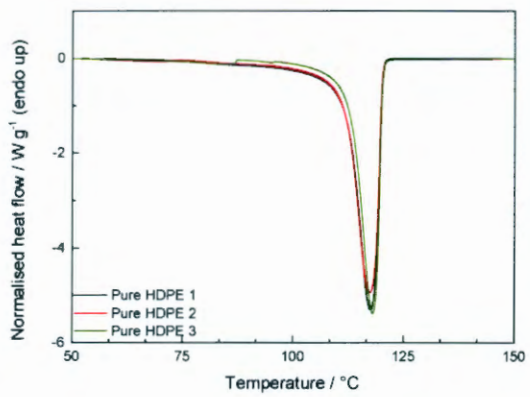
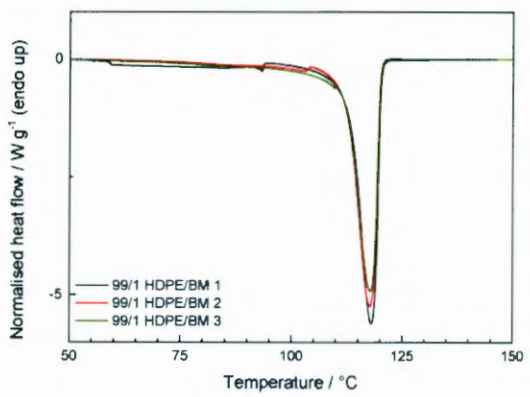
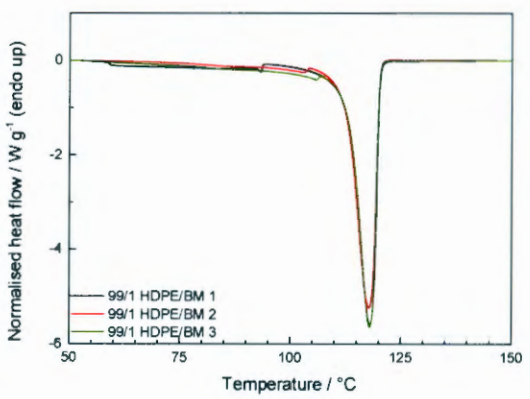
<tr><td> 
</td><td> 
</td></tr>
<tr><td>99/1 w/w HDPE/BM – unaged</td><td>99/1 w/w HDPE/BM – aged 36 weeks</td></tr>
<tr><td> 
</td><td> 
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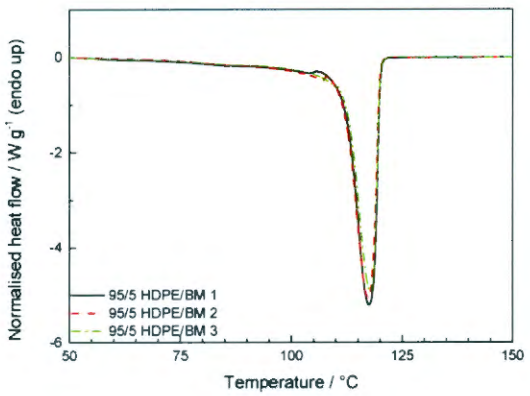
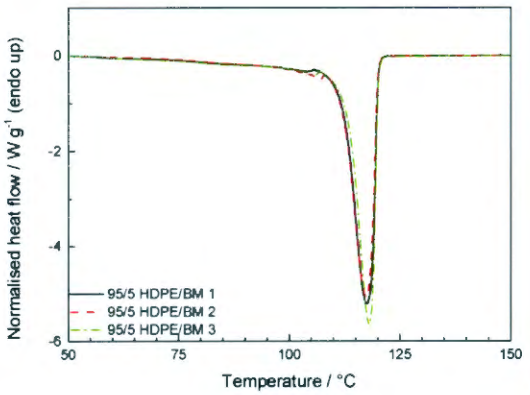
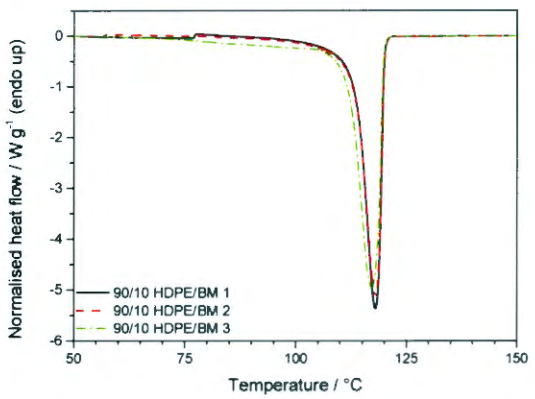
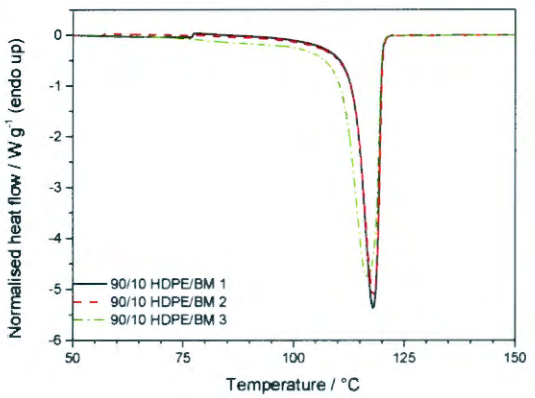
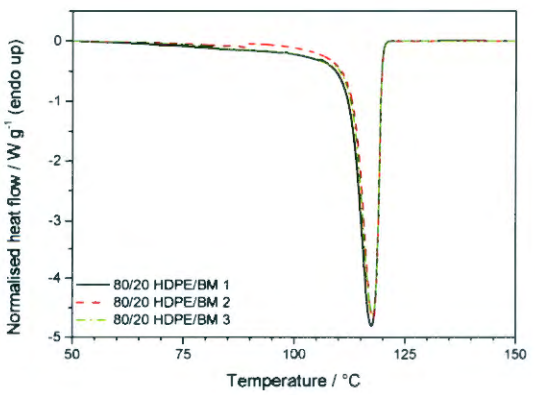
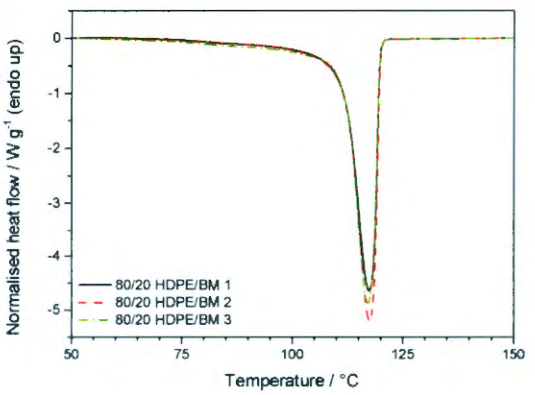
95/5 w/w HDPE/BM – unaged	95/5 w/w HDPE/BM – aged 36 weeks
	
90/10 w/w HDPE/BM – unaged	90/10 w/w HDPE/BM – aged 36 weeks
	
80/20 w/w HDPE/BM – unaged	80/20 w/w HDPE/BM – aged 36 weeks
	

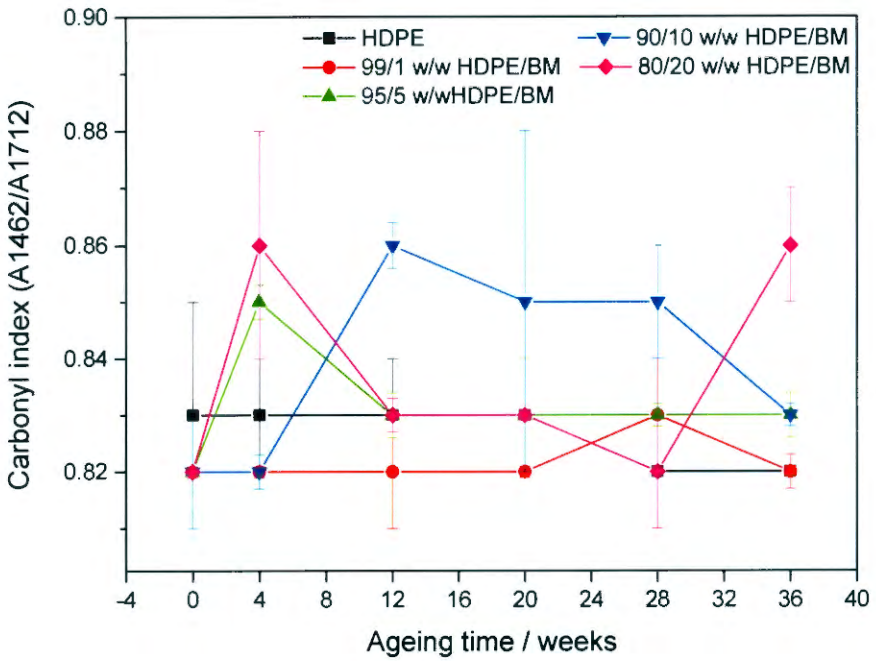


Figure A.3.2 Carbonyl index values of 0.2 mm films of all composites with ageing time

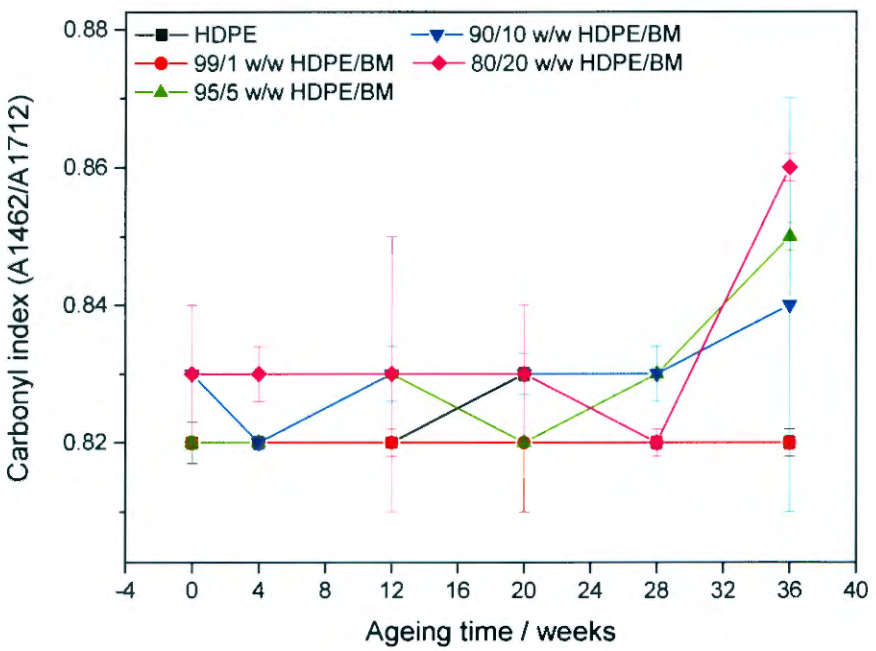


Figure A.3.3 Carbonyl index values of 0.7 mm films of all composites with ageing time

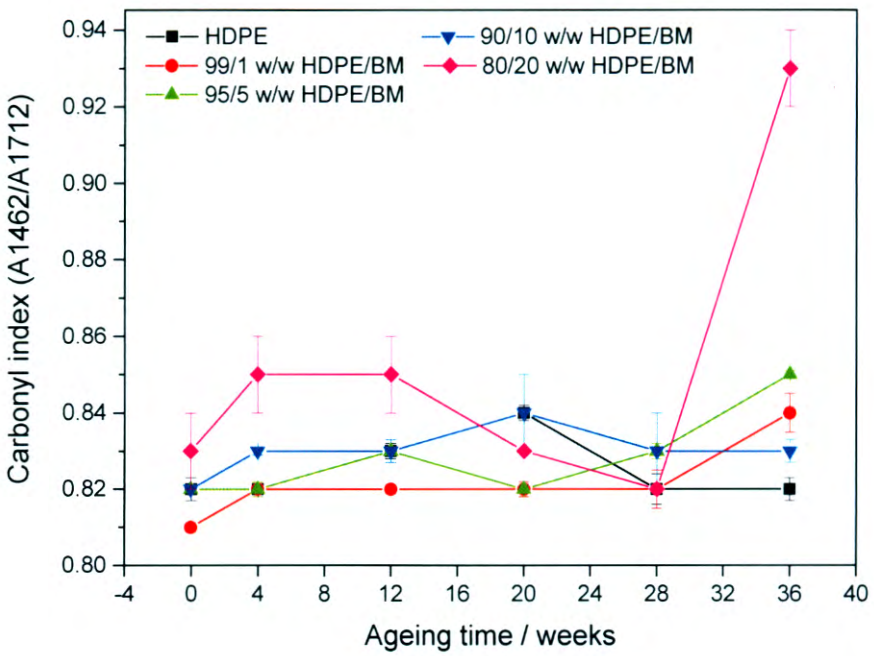
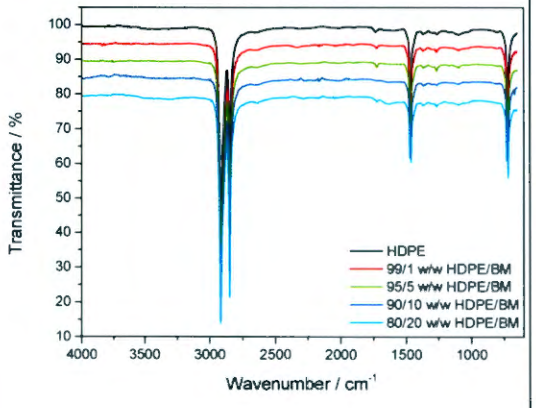
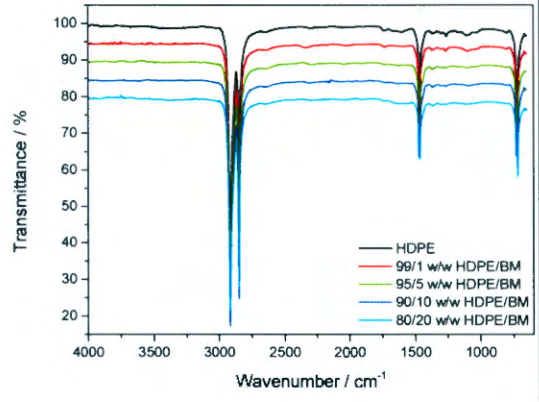
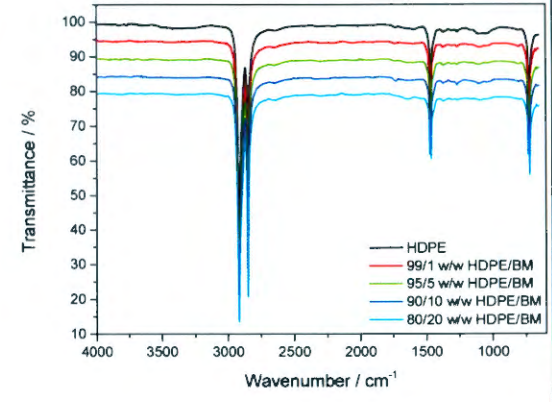
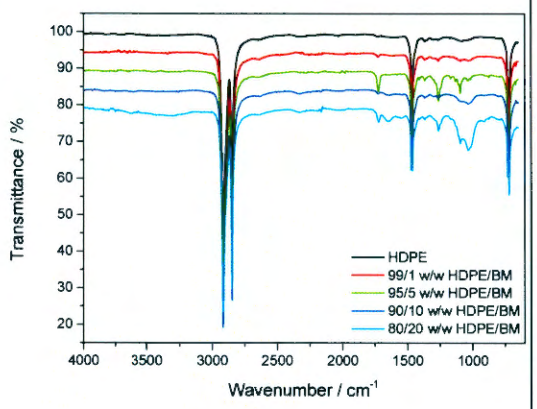
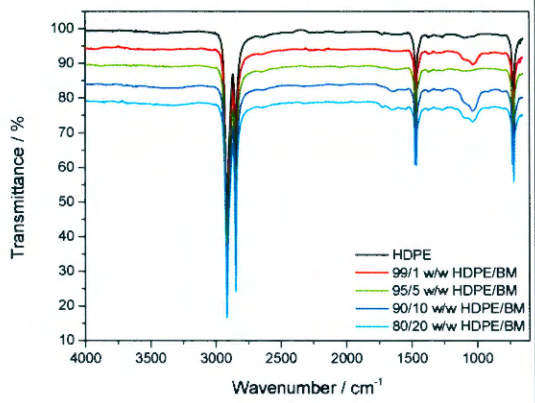
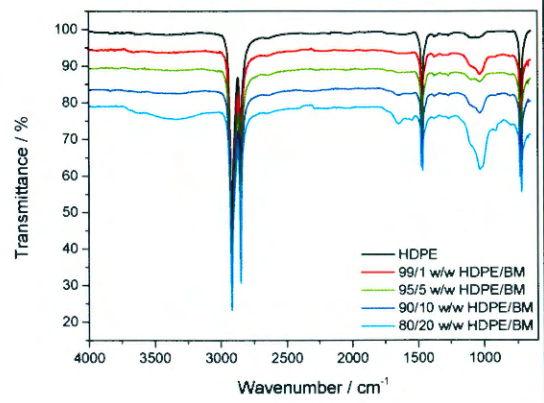
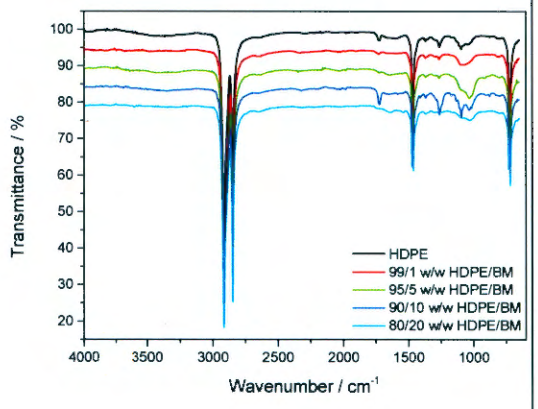
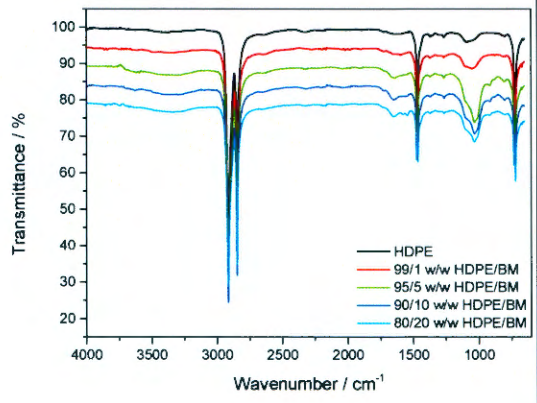
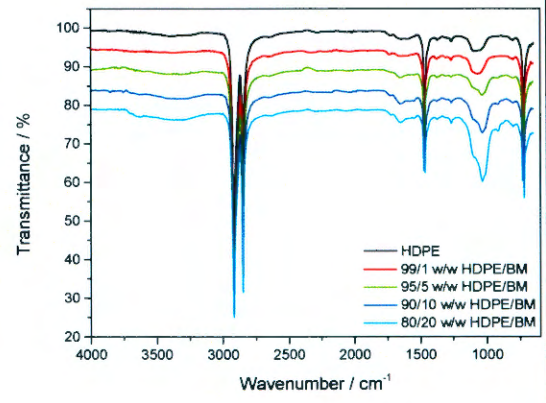


Figure A.3.4 Carbonyl index values of 1.0 mm films of all composites with ageing time

Table A.3.5 Table of FTIR graphs for all the composites, unaged and composites aged for 36 weeks

Ageing time	Composite film thickness: 0.2 mm	0.7 mm	1.0 mm
0 weeks (unaged)			

Ageing time	Composite film thickness		
	0.2 mm	0.7 mm	1.0 mm
4 weeks			
12 weeks			

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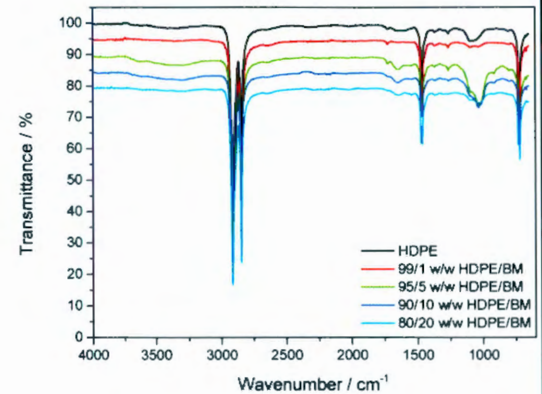
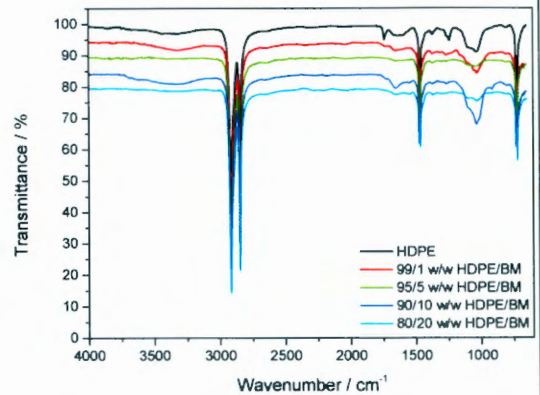
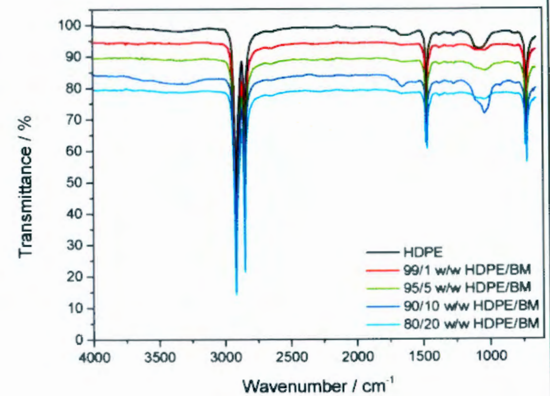
<tr><td></td><td>20 weeks</td><td> 
</td><td> 
</td><td> 
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	Composite film thickness		
	0.2 mm	0.7 mm	1.0 mm

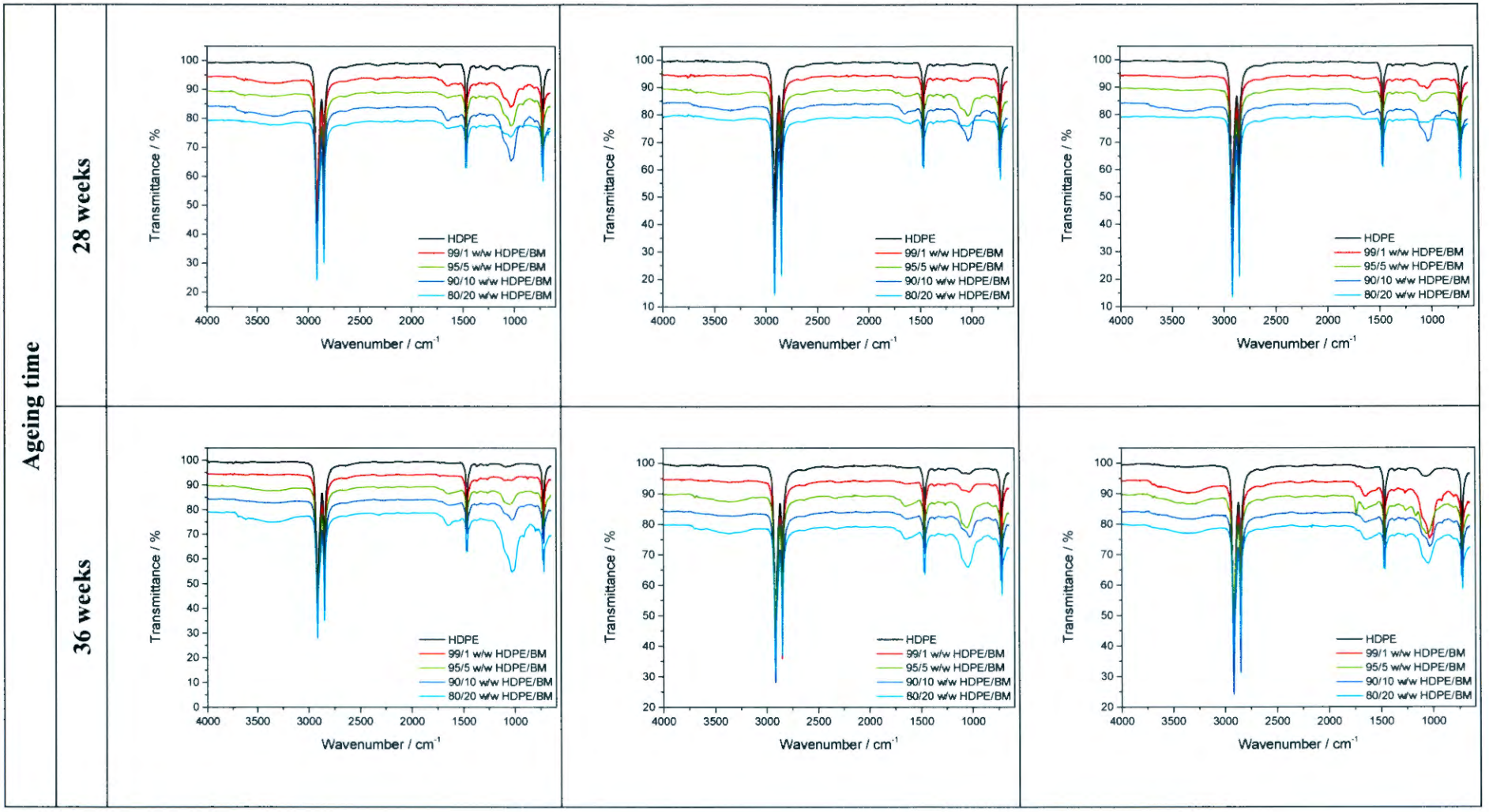
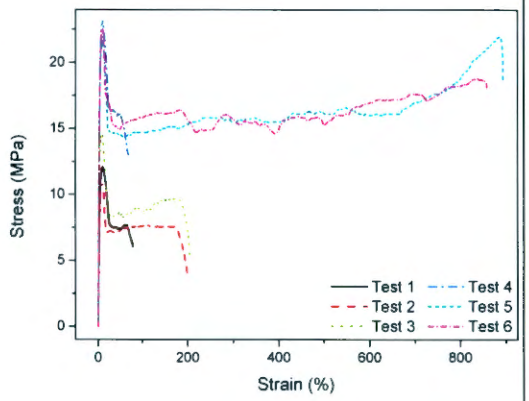
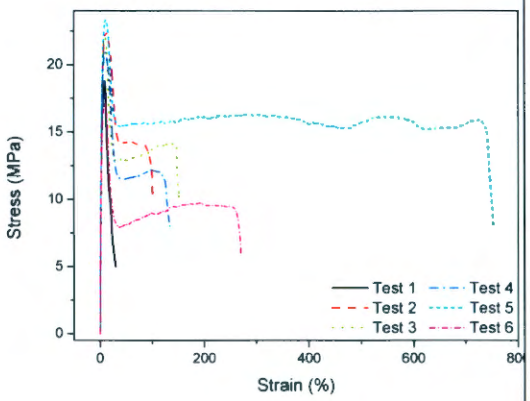
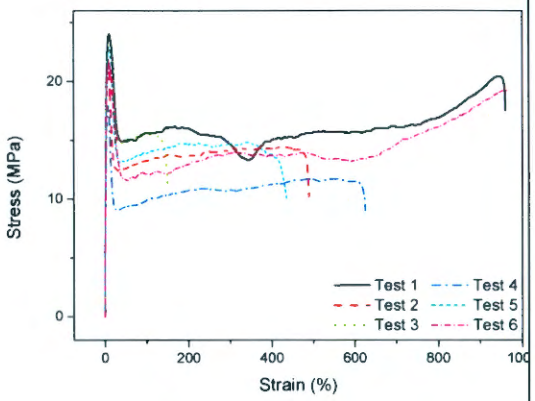
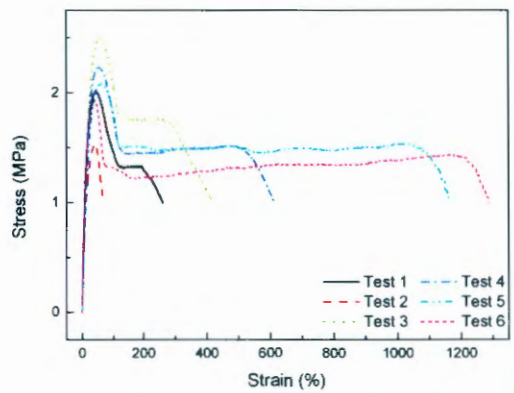
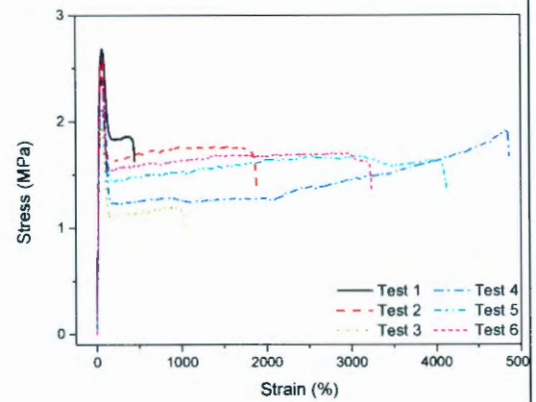
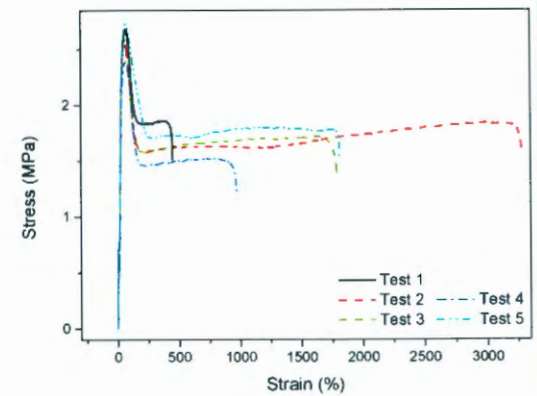
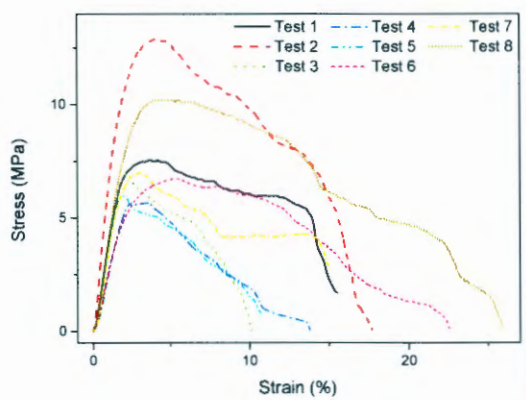
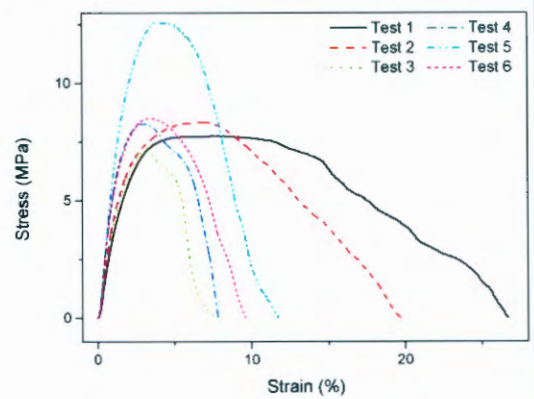
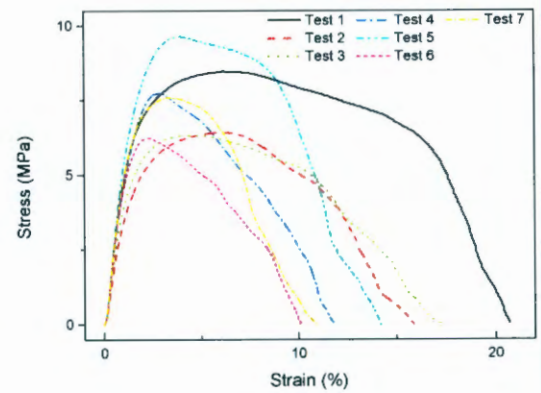
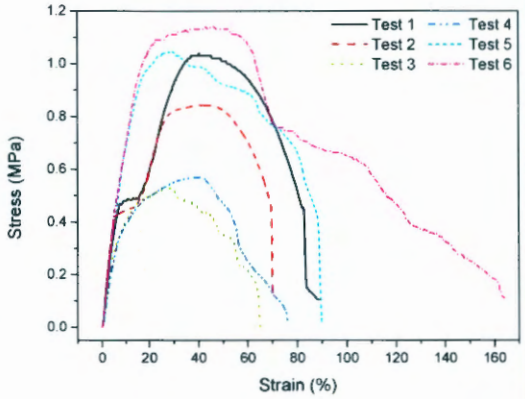
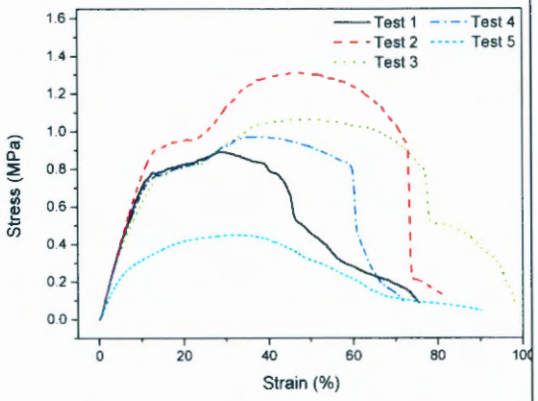
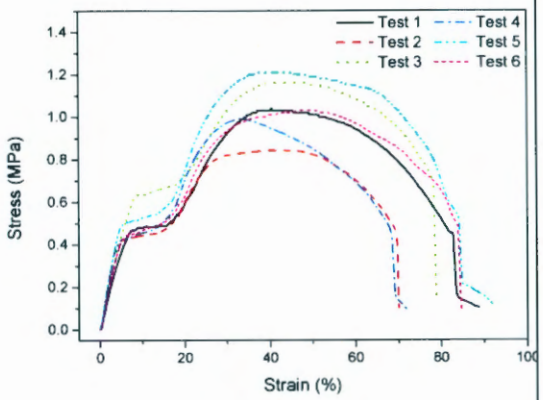


Table A.3.6 Table of stress-strain curves for pure HDPE and 80/20 w/w HDPE/BM composite films, unaged and composites aged for 36 weeks

Ageing time		Composite film thickness		
		0.2 mm	0.7 mm	1.0 mm
Pure HDPE	0 weeks			

		Composite film thickness		
		0.2 mm	0.7 mm	1.0 mm
Ageing time	Pure HDPE 36 weeks			
Ageing time	80/20 w/w HDPE/BM 0 weeks			

Ageing time	80/20 w/w HDPE/BM	Composite film thickness		
		0.2 mm	0.7 mm	1.0 mm
				

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