5-2010

BIODEGRADABLE POLYMER BLENDS AND COMPOSITES FROM PROTEINS-produced by animal co-product industry

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ABSTRACT

Development of new green materials from by-products of animal rendering industries would provide a substantial economic return to animal rendering processors. Meat and bone meal (MBM), one of the products of the rendering industry, has potential for numerous bio-based applications. This research focuses on fabrication of plastics blends made of MBM (Meat and bone meal) and UHMWPE (ultra high molecular weight polyethylene). We investigated thermal, morphological, water absorption and mechanical properties of the plastics. The plastics were compression molded and their properties were examined.

DSC thermographs of the blends indicated that the thermal properties of UHMWPE did not change drastically with increase in MBM content. The tensile strength, elongation of the blends decreased with MBM content where else modulus increased with increase in MBM. MBM/UHWMPE (30/70) blend was found to have the most reproducible and useful properties. Morphology of the blends showed a typical sea and island structure of immiscible blend. The effect of blend composition on water contact angle was also investigated. Contact angle decreased with increase in MBM.
DEDICATION

This thesis is dedicated to my parents, Joshua Muli and Beatrice Muli, my siblings, Anne Mutile Nzioki, Amos Mwatu Nzioki, Philip Kioko Nzioki and Joseph “Kamali” Nzioki for their love and support.
ACKNOWLEDGMENTS

I would like to pass my sincere gratitude to my advisor Dr. Igor Luzinov for all his support and for providing this opportunity to conduct this research. His guidance, encouragement, excitement, dedication, humor and trust have helped create this thesis. He has provided me with the vision for future career and what can be accomplished through biopolymers.

I would also like to thank my committee members Dr. Jian Luo, Dr. Bogdan Zdyrko and Dr. John Desjardins, for their time and contributions. I would like to specifically thank Dr. Zdyrko for his unrelenting help in the lab and for answering numerous questions.

Fehime Vatansever my gratitude goes out to you for your assistant in plastic processing and analysis and for never getting tired of lending a hand when I needed one.

I would also like to express my gratitude to my research group members for maintaining a great working atmosphere both in the office and in the lab James Giammarco, Michael Seeber, Fehime Vatanserver, Marius Chyasnavichyus, Yuri Galabura and Tugba Demir.

Finally I would also like to thank the Materials Science and Engineering lab technicians Stanley Justice, James Lowe, Robbie Nicholson and especially Kim Ivey for her relentless help with thermal and mechanical analysis.
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Polymers have provided a wide range of products in response to the increasing demand and the ever growing market for new materials. While polymer products demand has been based on synthesis of new polymers in the past, the focus has shifted to other approaches due to governmental restrictions, environmental and societal concerns. Scientist and researchers have shifted their focus to natural/biodegradable blends and composite materials. Biodegradable polymers have been instrumental in offering scientist and researchers a possible solution to pollution and waste disposal problems stemming from plastics disposal. Rising oil prices have also stimulated more interest in biodegradable and bio derived polymers.

The concept of blending biodegradable and conventional polymers to increase their biodegradability has attracted a wide interest and commercial utilization in recent years. Polymer-polymer composites and polymer blends combine some important characteristics of each blend constituents. Generally polymer blends are produced by mechanically blending polymers in processing equipment.

The main objective of this project was to process and characterize plastics from protein rich meat and bone meal (MBM) and also to investigate the possibility of blending MBM with ultra high molecular weight polyethylene (UHMWPE); UHMWPE was chosen for its good mechanical properties.
Chapter 2. to this end, provides an overview of the evolution of biodegradable polymers and composites/blends. This chapter also explores sources of natural biodegradable polymers and their applications. And lastly biodegradable polymers as components in composite blends are also explored and classified.

Chapter 3 provides descriptions of the experimental techniques used in this work.

Chapter 4 focuses on preparation of plastics blends from MBM/UHMWPE with non defatted MBM. Thermal and mechanical properties are analyzed, thermal analysis include: degradation temperatures and melting temperatures of both neat materials and blends. Mechanical properties explored include: tensile modulus, storage modulus strength and elongation.

Chapter 5 explores the effect of defatting MBM and blending it with UHMWPE on plastics blends mechanical properties. Thermal analysis was performed to determine if the blending caused a change in melting temperatures and crystallinity of UHMWPE. Mechanical properties of the blends were determined and analyzed with existing models to determine level of adhesion in the blended materials. Blend morphology analysis was also performed to determine if phase separation present in the blends. Water absorption analysis was performed to determine its effect of moisture on plastics mechanical properties.

Chapter 6 and 7 provides summary, conclusions and gives recommendations on future work on this research.

In conclusion, this thesis provides the fundamentals and characterization of plastics blends from MBM and UHMWPE and their potential applications.
CHAPTER TWO
LITERATURE REVIEW

This research focuses on fabricating blends from biopolymers with emphasis on rich in proteins meat and bone meal (MBM) and describing the properties of plastics manufactured from them. Therefore; an overview and theoretical information pertaining biodegradable materials is presented.

2.1: Biodegradable polymers

Littering and waste disposal with regard to environmental pollution has created urgency and the need to develop biodegradable materials that have comparable properties with current polymeric materials at an equivalent or lower cost. Currently a number of biodegradable polymers are derived from both synthetic and natural sources [1].

Polymers from renewable resources have attracted a lot of attention in the past two decades. Mainly, due to the environmental concerns and the realization that petroleum resources are diminishing [2]. Renewable and sustainable biodegradable materials can reduce the use of petroleum reserves and also reduce dependence on foreign oil that has led to political instability in certain countries due to corruption [2]. Biodegradable polymers have offered scientists a possible solution to waste-disposal problems associated with traditional petroleum–derived plastics. Polymers from natural resources can be improved via blending and formation of composites, if their properties are not acceptable [3].
For instance, it is recognized that biodegradable polymers and composites plastics are a good choice for the packaging industry because packaging materials are widely used and disposed off after a short period of time [4]. Therefore, due to their degradability the bio-plastics are more suited for the packaging applications than conventional plastics which persist for years after the disposal. The typical life cycle of biodegradable polymers is represented in Figure 2.1 [5, 6].

![Figure 2.1: Life cycle representation of biodegradable polymers [5, 6].](image-url)
The study of utilization of naturally occurring polymers is an ancient science which began with paper, silk, skin and bone arts that can all be found in museums all over the globe [7]. However the availability of petroleum–based products at lower prices diminished or slowed the use of natural polymers and this move has proven in many aspects disastrous for the environment and the economy. Until the energy crisis in 1970 natural polymer synthesis had no incentives, but the crisis was an incentive to seek naturally occurring sustainable polymers and work on improvements of their mechanical properties [8]. Therefore, natural polymers have evolved rapidly and modern technology has made their use more viable. These new technologies provide powerful tools to develop new materials for various applications [9].
2.2: Composites

Composites are manufactured by combining two materials, a matrix and a filler, and each material retains their identity [10]. Composites have been also traditionally known to comprise of polymer matrix and fiber filler as reinforcing materials. In general, composites can be classified as follows see Figure 2.2.

**Figure 2.2:** Classification of composites [11].

Composites have encompassed almost all material domains. All synthetic polymers can be used as matrices. Inorganic fillers such as glass, carbide and silicium have been used as fillers. Compared to the inorganic fillers natural fibers present some very well known advantages such as: lower density and lower prices. They are also less abrasive to the processing equipment, harmless, biodegradable and renewable [1, 2, 12, 13]. The important feature of composite materials is that they can be tailored to meet different requirements.
Composites are of great attraction because they combine material properties in ways that are not found in nature. Composites properties include: lightweight structures with high stiffness [14]. Fiber reinforced composites usage began in the year 1908 with the incorporation of cellulose in phenolics resulting into fiber reinforced plastics, this was later extended to urea and melamine and further developments were evident in 1940 with glass fiber incorporation into polyesters [15].

2.2.1 Natural fibers as reinforcing fillers for composites

In the past few decades research and engineering has showed more interest in utilizing fibers as additives in composites. Fibers used as fillers include (aramid, carbon and glass) [16]. Fiber reinforced composites have diverse applications. Figure 2.3.

![Figure 2.3](image-url)

**Figure 2.3:** Fiber reinforced composites used in 2002 (Adapted from Plast. News August 2002) [17].
Biodegradability has called upon the use of natural fibers as fillers due to environmental and disposal concerns for non biodegradable materials. Cellulose is the main vegetable fiber used in composites. Global market for natural fiber composites was 771 million kg in 2002 and has grown extensively. One of the most important fields of fiber composites applications is in the automotive industry [13, 18].

Natural fibers are widely used as well in polymeric materials to improve mechanical properties. These fibers can be classified as bast, leaf or see-hair fibers. Natural fibers properties vary depending on: origin, quality of the plants locations, the age of the plant and the preconditioning. The most common known natural fibers include (i) leaf: sisal, pineapple, leaf fiber (PALF) and henequen (ii) bast, flax, ramie, kenaf/mesta, hemp and jute (iii) seed: cotton (iv) fruit: coconut husk, i.e., coir [7, 8, 19, 20]. All important natural fibers are listed in Table 2.1.
Table 2.1: List of important natural fibers and their origin [1].

<table>
<thead>
<tr>
<th>Fiber Source</th>
<th>Species</th>
<th>Origin</th>
</tr>
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<tbody>
<tr>
<td>Abaca</td>
<td>Musa textilis</td>
<td>Leaf</td>
</tr>
<tr>
<td>Bagasse</td>
<td>-</td>
<td>Grass</td>
</tr>
<tr>
<td>Bamboo</td>
<td>(&gt; 1250 species)</td>
<td>Grass</td>
</tr>
<tr>
<td>Banana</td>
<td>Musa indica</td>
<td>Leaf</td>
</tr>
<tr>
<td>Broom root</td>
<td>Muhlenbergia macroura</td>
<td>Root</td>
</tr>
<tr>
<td>Cantala</td>
<td>Agave cantala</td>
<td>Leaf</td>
</tr>
<tr>
<td>Caroa</td>
<td>Neoglaziovia variegate</td>
<td>Leaf</td>
</tr>
<tr>
<td>China jute</td>
<td>Abutilon theophrasti</td>
<td>Stem</td>
</tr>
<tr>
<td>Coir</td>
<td>Cocos nucifera</td>
<td>Fruit</td>
</tr>
<tr>
<td>Cotton</td>
<td>Gossypium sp.</td>
<td>Seed</td>
</tr>
<tr>
<td>Curaua</td>
<td>Anans erectifolius</td>
<td>Leaf</td>
</tr>
<tr>
<td>Date palm</td>
<td>Phoenix Dactylifera</td>
<td>Leaf</td>
</tr>
<tr>
<td>Flax</td>
<td>Linum usitatissium</td>
<td>Stem</td>
</tr>
<tr>
<td>Hemp</td>
<td>Cannabis sativa</td>
<td>Stem</td>
</tr>
<tr>
<td>Henequen</td>
<td>Agave fourcrydes</td>
<td>Leaf</td>
</tr>
<tr>
<td>Isora</td>
<td>Helicteres isora</td>
<td>Stem</td>
</tr>
<tr>
<td>Istle</td>
<td>Samuela carnerosana</td>
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<td>Jute</td>
<td>Corchorus capsularis</td>
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<td>Kapok</td>
<td>Ceiba pentranda</td>
<td>Fruit</td>
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<td>Kenaf</td>
<td>Hibiscus cannabinus</td>
<td>Stem</td>
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<tr>
<td>Kudzu</td>
<td>Pueraria thunbergiana</td>
<td>Stem</td>
</tr>
<tr>
<td>Mauritius hemp</td>
<td>Fucraea gigantean</td>
<td>Leaf</td>
</tr>
<tr>
<td>Nettle</td>
<td>Urtica dioica</td>
<td>Stem</td>
</tr>
<tr>
<td>Oil palm</td>
<td>Elaeis guineensis</td>
<td>Fruit</td>
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<td>Piassava</td>
<td>Attalea funifera</td>
<td>Leaf</td>
</tr>
<tr>
<td>Pineapple</td>
<td>Ananus comosus</td>
<td>Leaf</td>
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<tr>
<td>Phormium</td>
<td>Phormium tenas</td>
<td>Leaf</td>
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<tr>
<td>Roselle</td>
<td>Hibiscus sabdariffa</td>
<td>Stem</td>
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<td>Ramie</td>
<td>Boehmeria nivea</td>
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<td>Sanservieria (Bowstring hemp)</td>
<td>Sansevieria</td>
<td>Leaf</td>
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<tr>
<td>Sisal</td>
<td>Agave sisilana</td>
<td>Leaf</td>
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<tr>
<td>Sponge gourd</td>
<td>Luffia cylindrica</td>
<td>Fruit</td>
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<td>Straw (Cereal)</td>
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<td>Sun hemp</td>
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<td>Stem</td>
</tr>
<tr>
<td>Cadillo/urena</td>
<td>Urena lobata</td>
<td>Stem</td>
</tr>
<tr>
<td>Wood</td>
<td>(&gt; 10,000 species)</td>
<td>Stem</td>
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</table>
Advantages of biofibers over traditional non-biodegradable fillers/fibers such as fiber glass, talc and mica are: low cost, low density, high toughness, acceptable specific strength, reduced tool wear, reduced dermal and respiratory irritation, good thermal properties, ease of separation, enhanced energy recovery and biodegradability [8]. Natural fibers have several drawbacks in comparison to glass fibers that are know to have good mechanical properties and are of low cost as indicated in Table 2.2 [16].

Drawbacks associated with natural fibers include: poor wettability, incompatibility with some polymer matrices, moisture absorption and low processing temperatures due to the possibility of fiber degradation or possibility of volatile emission that could affect the composite performance [16]. Researchers have explored manipulation of natural fibers to obtain desired properties. Natural fibers have found their way to the market in applications such as automotive components that were previously manufactured from glass composites [16, 21, 22].

**Table 2.2: Comparison between natural and glass fibers** [16].

<table>
<thead>
<tr>
<th></th>
<th>Natural fibers</th>
<th>Glass fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Low</td>
<td>Twice that of NF</td>
</tr>
<tr>
<td>Cost</td>
<td>Low</td>
<td>Low, but higher than NF</td>
</tr>
<tr>
<td>Renewability</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Recyclability</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Energy consumption</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Distribution</td>
<td>Wide</td>
<td>Wide</td>
</tr>
<tr>
<td>CO₂ neutral</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Abrasion to machines</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Health risk when inhaled</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Disposal</td>
<td>Biodegradable</td>
<td>Not biodegradable</td>
</tr>
</tbody>
</table>
Fiber adhesion to polymer matrix is the main problem facing utilization of natural fibers for composites. A lack of strong filler to matrix adhesion reduces composite performance and limits applications due to decline in mechanical properties [18]. Adhesion properties have been studied to make improvements. These improvements include: physical treatments (cold plasma treatment, corona treatment) and chemical treatment (maleic anhydride, organosilanes, isocynates, sodium hydroxide, permanganate and peroxide) [18, 23-25].
2.3: Biodegradable/Biobased polymers classification

Depending on the synthesis process biopolymers have been classified into three categories and these include: [26, 27].

- Polymers from biomass.
- Polymers from microbial synthesis.
- Chemically and conventionally synthesized from biomass monomers.

**Figure 2.4:** Schematic representation of biobased polymers based on their origin and method of production [26].
2.4: Biodegradability of polymers

The American Society for Testing and Materials (ASTM) and the International Standards Organization (ISO) have defined degradable plastics to be those that undergo significant change in chemical structure under specific conditions [7]. The changes that the plastic undergo result into loss of physical and mechanical properties in comparison with the established standards [7].

The term biodegradable plastic is defined as plastic that will degrade from the action of naturally occurring microorganism such as bacteria, fungi e.t.c over a period of time [5]. In recent years there has been increased interest on biodegradable polymer products from agricultural products [28]. Waste disposal problems and sustainability of resources have fueled intensified research on bioplastics. Blending of synthetic and natural polymers has become an increasing trend as an alternative for utilization of wholly natural polymers. There are potential applications for which bioplastics can be used for instance cutlery, flower pots and food trays [26].

Bioplastics are made through two processes either dry (melt process) or wet process (aqueous process) [15]. The wet process requires biopolymers dispersion in a film-forming solution and this has been successfully applied to edible film coatings. The dry melt process capitalizes on the thermoplastic properties of biopolymers and has been successfully used in edible coatings as well. Wet process has a drawback because the solvents used are not environment friendly thus making the melt process a better option in manufacturing of bioplastics [15].
Biopolymers degrade through enzymatic action of bacterial, fungi, algae, and other living organisms [8, 26]. The end products of degradation are carbon dioxide, new biomass and water. Degradation comparison is difficult to establish due to different composting conditions such as humidity and temperature cycle [4]. Some general rules are applicable in estimating the evolution of biodegradability and these include: an increase in hydrophobic character, molecular weight, crystallinity of the size of spherulites decrease biodegradability and on the contrary, the presence of polysaccharides favors degradation [29].

Biodegradability is not only observed due to origin of its chemical structure and degrading environment. There are other contributors such as polymer morphology, radiation and chemical treatments, and molecular weight [29]. In order to synthesize polymer to degrade by enzyme catalysis the polymer chains must be flexible enough to fit into the active site of the enzyme [29].

Proteins (natural polymers) differ from synthetic polymers in the essence that proteins do not have equivalent repeating units along the peptide chains. The irregularity results in protein chains being less likely to crystallize and this is attributed to the biodegradability in proteins [26]. Numerous studies have been carried out to determine the effects of molecular weight on biodegradation. It is established that microorganisms produce both exoenzymes and endoenzymes and findings were that plastics remain immune to microbial attack as long as the molecular weight remains high [26].

Figure 2.5 represents the life cycle of compostable polymers.
Figure 2.5: Schematic representation of the life cycle of compostable polymers [8, 17].
2.5: Protein Plastic

2.5.1: Protein denaturing and structurization of plastic

Proteins are biopolymers that consist of combinations of polar and apolar amino acids, along the main chain. There are various side chains attached to the amino acids [30, 31]. The physicochemical properties, such as charge, solubility and chemical reactivity are dependent on the chemical nature of the side chains [32]. The amino acid residues are able to form numerous intermolecular bonds and interactions, resulting into a broad range of protein functionalities. The amino acid sequence is the primary of the polypeptide protein chain that forms α helices and β sheets making the secondary structure. Tertiary or three dimensional structures consist of an arrangement of folded polypeptide chain with secondary structure segments aligned in a three dimensional fold form. Further complex arrangement of peptide chains are referred to as quaternary structures [33]. Figure 2.6 is a schematic representation of the protein structure.
Figure 2.6: Schematic representation of the protein structure [33].

The monodispersity and precise definition of primary structure of proteins gives them unique secondary and tertiary structures that are required for their hierarchical organization and biological function. Proteins however, have limitations in the essence that they can be toxic, can potentially be easily degraded in unpredicted ways and readily lose their bioactivity [34, 35]. Denaturing of protein can occur under numerous physical conditions such as high temperature, high or low pH and high pressures [36-38].
Fitter [39] stated that thermal unfolding of proteins at high temperatures is a result of strong increase of entropy change that lowers Gibbs free energy change of unfolding transition ($\Delta G_{\text{unf}} = \Delta H - T \Delta S$). Main contributors of entropy change being conformational entropy of polypeptide chain itself and ordering of water molecules around hydrophobic side chains of the protein [39].

Some possible unfolding intermediates include partial separation of two domains with exposed hydrophobic surface have been observed during urea denaturization [38, 40]. Hawley calculated the Gibbs free energy ($\Delta G$) of denatured and undenatured protein and obtained a second order curve before denaturation conditions ($\Delta G=0$). The calculation turned into an elliptical curve for proteins. Figure 2.7 [41, 42].

![Figure 2.7: Schematic representation of elliptic phase diagram of protein denaturation.](image)

Letters denoting mode of denaturization: p-Pressure, h-Heat and c-Cold denaturation [41, 42].
The phase diagram above is a description of the conditions under which the protein is in its native or denatured state at a given temperature and pressure. The difference between temperature and pressure denaturization is very pronounced and the difference is evident not only in conformation of the polypeptide chain but also in the difference of the intermolecular interactions of proteins in the denatured state [42]. These studies have been carried out using Fourier transform spectroscopy. Temperature denatured proteins develops an extensive intermolecular hydrogen bond network, but this network is absent in pressure denatured proteins [43, 44].

Fluorescence studies by Wiedersich et al. [45] on temperature and pressure dependence of protein stability from the absorption and emission spectra of free fluoriscein and FluA fluoriscein complex. It was found that at room temperature and pressure the residue of fluoriscein of native protein was negligible. Fitter [39] utilized neutron spectroscopy to analyze α-amylase and conformational entropy changes showed significant increase upon heating and therefore contributed to thermal unfolding [39].

Comparative Fourier transform infrared spectroscopy was also utilized by Meersman et al. [46] to study cold, pressure and heat induced unfolding and aggregation of myoglobin. It was conclusive that cold denaturation did not give rise to intermolecular aggregation bands that are typical for the infrared spectra of many heat-unfolded proteins. Also it was conclusive that cold and pressure unfolding are different from that of the heat unfolding [46].
2.5.2 Plasticization thermodynamics of proteins

Plasticization decreases internal friction in a material. Plasticizing effect can be described in terms of lowering fracture strength, elastic modulus, and viscosity of a biopolymer [47]. There are three theories that have been proposed to account for plasticization mechanism: (i) lubricity theory, the plasticizer acts as a lubricant that facilitates the movement of the macromolecules over each other, hence reducing the internal resistance to deformation; (ii) gel theory, the function of the plasticizer is to disrupt polymer-polymer interactions due to internal forces such as van der waals, ionic and, hydrogen bonds; (iii) free volume theory, the plasticizer suppresses the glass transition temperature by increasing the polymers free volume. The fundamental concept pertaining these theories is that the plasticizer can interpose itself between the polymer chains and decrease the forces that bind the chains together [48, 49].

Proteins stability is associated to intermolecular attractions hydrogen bonds and nonpolar interactions, plasticizers should be polar and must also be good solvents for the protein. The plasticizer is required to increase flexibility and should be of low molecular weight, high boiling points and compatible with the polymers [47, 49-51]. Polyols are often cited as the best plasticizers for proteins due to their ability to reduce intermolecular bonding while increasing intermolecular spacing [52].
Mo et al. [48] investigated the plasticization of soy protein polymer by polyol based plasticizers. Results indicated that thermal properties of the soy protein plastics with propylene glycol were depressed to a large degree. Also the morphology of the fractured surface of the soy proteins changed from brittle fracture for the unplasticized to ductile fracture for the plasticized soy protein plastics. Water absorption for all the plasticized soy plastic polymers was lower than that of unplasticized soy protein plastics [48].

In another study, Mo and Sun [53] used urea to modify soy isolate protein to form soy protein plastic. They found that temperatures of denaturation and enthalpies of denaturation of modified soy protein decreased with increase in urea concentration above 1M. Tensile strength and Young’s modulus of the molded plastics increases as urea concentration increased and reached their maximum at a urea concentration of 8M. Both storage modulus and glass transition temperature of the modified soy protein also increased with increased concentration of urea. Plastics made with 2M urea concentrations showed improvements in elongation, tough fracture behavior and water resistance. In this case the urea functioned as a plasticizer, a denaturant as well as filler for soy protein [53].
Audic et al. [51] investigated the influence of plasticizers and crosslinking on the properties of biodegradable films made from sodium caseinate. They found that among the different polyol-type plasticizers used, glycerol and triethanolamine (TEA) were the most efficient for the improvement of mechanical properties. Further, crosslinking between formaldehyde (HCHO) and free of amino groups (ε-NH₂) of sodium caseinate increased water resistance on TEA films and also optimal mechanical properties were obtained.

Sanchez et al. [50] studied the effect of different plasticizers on the mechanical properties and surface properties of wheat gliadin films. Five polyols of ethylene glycols series and glycerol were compared as plasticizers. They founds that glycerol containing protein solutions had a higher viscosity than others. Also at equal concentrations in films they found that glycerol and tetra-ethylene glycol were more efficient than the other plasticizers used. Tensile strength was found to always be lower than that of synthetic polymer films and a negative relationship, independent of the plasticizing molecules used, was found between tensile strength and elongation at break of gliadin films. Surface hydrophobicity was found to be high for the films and no influence of plasticizers was observed [53].

Gioia et al. [49] investigated the effect of some polar and amphiphilic plasticizers on corn protein base-thermoplastic resins and found that the plasticizing efficiency at equal molar content was proportional to the molar weight and inversely proportional to the percentage of hydrophilic groups of the plasticizer. The migration rates of the plasticizers in the polymers were related to physicochemical characteristics [49].
2.6: Polymer blending

Polymer blending is an economical technique geared toward modifying polymer properties. This strategy is usually cheaper and less time consuming than development of new monomers for polymer synthesis [54]. Blending usually takes place in processing machines thus existing equipment can be utilized and an additional advantage of the polymer blends is a wide range of material properties that can be obtained by altering the blend composition. Properties of resulting materials may be tailored to meet requirements of customers or specific applications [55, 56].

Polymer blends are defined as physical mixtures of structurally different homopolymers/copolymers [57]. At thermodynamic equilibrium, a mixture of two polymers in the amorphous state may exist as a single phase of mixed segments and hence the blend is said to be homogenous on a microscopic scale and is considered miscible. When the mixture of two polymers exhibit separate phases consisting of individual components the blend is heterogeneous and on a microscopic scale its immiscible. Immiscible polymers may be considered compatible if they exhibit good mechanical properties. Mechanical properties of blends and thermal characterization is the well known method to determine their miscibility and compatibility [58, 59].
Miscibility in polymers in the amorphous state is detected by the presence of a single glass transition temperature ($T_g$). For ideal systems the relationship between $T_g$ and the composition of the blend is predicted by several equations, for instance by the Fox equation [60, 61].

$$\frac{1}{T_g(\text{blend})} = \frac{W(1)}{T_g(1)} + \frac{W(2)}{T_g(2)}$$  \hspace{5cm} (2.1)

Where $T_g(\text{blend}), T_g(1)$ and $T_g(2)$ are the $T_g$ of the blend, Polymer 1 and Polymer 2, and $W(1)$ and $W(2)$ are the weight fractions of polymer 1 and 2 respectively. The properties of miscible polymers in general follow the so called mixing rule, Figure 2.8.

**Figure 2.8:** Properties of polymer blends
The properties of immiscible blends are controlled by the morphology and the degree of compatibility of the polymers. The morphology of the immiscible blends vary depending of viscosity, viscosity ratio of both polymers at the blending temperature, composition, interfacial modification, shear stress and processing conditions. The degree of compatibility on the other hand is controlled by polymer to polymer interfacial interactions which are modified by addition of compatibilizers or processing conditions [60-62]. The final properties of immiscible compatible blends may follow the “mixing rule” or even demonstrate the synergistic effect Figure 2.8.

Verhoogt et al. [57] studied polymer blends containing poly (3-hydroxyalakanoate)s and discovered that the crystallization behavior of the PHA was influenced by both the miscible and immiscible components. The degradability was mostly controlled by the blend morphology [57].

Other studies have included compatibility and mechanical properties of blends of polystyrene with biodegradable polyester such as polycaprolactone (PCL), poly-lactic acid (PLA) and eastar bio ultra (EBU). Bireshaw et al. [63] concluded that tensile properties varied among the polyester blends due to bulk properties of the biodegradable polyesters.
Kadla et al. [61] studied lignin based polymer blends and their intermolecular interactions with synthetic blends and thermal analysis revealed miscible blend behavior in lignin blends containing poly (ether oxide) (PEO) and polyethylene terephthalate (PET), whereas poly-vinyl-alcohol (PVA) and polypropylene (PP) were immiscible hence coming to the conclusion that intermolecular bonding especially hydrogen bonding has greater influence on blend properties [61].

Blending is not only limited to thermoplastics. Thermosetting material blends are also available. Tatara et al. [64] studied compression molding of phenolic resin and corn based distillers dried grains with solubles (DDGS). Blends from phenolic resin and DDGS were found to be of reasonable mechanical strength and the recommendation of coupling agents and other additives was suggested to improve mechanical properties.
2.7: Conclusions

Green materials are a wave of the future. There is a great opportunity in developing new bio-based products. Environmental regulations and ethical concerns have triggered the search for materials that are environment friendly. The incorporation of bio-resources in composite materials can reduce the dependency on petroleum reserves.

In order to be competitive, biodegradable materials must have the same desirable properties as obtained from conventional plastics. One of the main disadvantage of biodegradable polymers is they are hydrophilic and hence produce undesired mechanical properties under wet environment. Existing biodegradable plastics products physical properties and formulations should be further researched and modified so that degradation rate can be easily manipulated.

Natural fibers are of basic interest due to their many advantages from the point of weight and fiber matrix adhesion. Existing biodegradable polymers are mainly blended with different materials with the aim of cost reduction and tailor the product for specific applications.

The most important factors to the formation of a successfully biodegradable industry include cost reduction as well as public acceptance.
2.8: References:


3.1. Materials

Meat and bone meal (MBM) proteins from animal rendering plant and ultra high molecular weight polyethylene (UHMWPE) (867998 MJ, Sigma Aldrich) 180 micron powder were used to develop biodegradable polymer blends. The chemical structure of PE is represented in Figure 3.1. UHMWPE is synthesized from ethylene monomers via polymerization of ethylene gas, Figure 3.2 [1]. These molecules of polyethylene are of several orders in magnitude longer than high density polyethylene due to their synthesis that is based on organotitanate catalysis. UHMWPE is similar to HDPE differing primarily on the length of its molecular chains. Its average molecular weight is 10-100 times greater than HDPE. Typical mechanical properties of UHMWPE are presented in Table 3.1.

Figure 3.1: Chemical structure of polyethylene.
**Figure 3.2:** UHMWPE polymerization mechanism with Ziegler Natta catalyst [1].
Table 3.1: Typical properties of virgin UHMWPE [1].

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Typical Values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanical</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>0.926–0.934</td>
</tr>
<tr>
<td>Bulk density</td>
<td>g/cm³</td>
<td>0.350–0.500</td>
</tr>
<tr>
<td>Tensile strength @ yield</td>
<td>MPa</td>
<td>20–22</td>
</tr>
<tr>
<td>Tensile strength @ fail</td>
<td>MPa</td>
<td>41–44</td>
</tr>
<tr>
<td>Elongation @ fail</td>
<td>%</td>
<td>350–450</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td></td>
<td>~0.4</td>
</tr>
<tr>
<td>Izod impact strength</td>
<td>kJ/m²</td>
<td>no break</td>
</tr>
<tr>
<td>single 45° notch</td>
<td></td>
<td>≥100</td>
</tr>
<tr>
<td>double 15° notch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>MPa</td>
<td>1050</td>
</tr>
<tr>
<td>Hardness</td>
<td>Shore D</td>
<td>62–66</td>
</tr>
<tr>
<td>Coefficient of friction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dry</td>
<td></td>
<td>0.10–0.22</td>
</tr>
<tr>
<td>wet</td>
<td></td>
<td>0.05–0.10</td>
</tr>
<tr>
<td>Relative solution viscosity</td>
<td>dL/g</td>
<td>2.3–3.5</td>
</tr>
<tr>
<td><strong>Thermal</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystalline melting range</td>
<td>°C</td>
<td>135–138</td>
</tr>
<tr>
<td>Linear thermal expansion</td>
<td>K⁻¹ (20–100°C)</td>
<td>~0.0002</td>
</tr>
<tr>
<td>Latent heat of fusion</td>
<td>J/g</td>
<td>170–180</td>
</tr>
<tr>
<td>Specific heat</td>
<td>J/(g·K) at 20°C</td>
<td>1.84</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>W/(m·K) at 20°C</td>
<td>0.42</td>
</tr>
<tr>
<td>Decomposition temperature</td>
<td>°C</td>
<td>~300</td>
</tr>
<tr>
<td><strong>Electrical</strong></td>
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</tr>
<tr>
<td>Volume resistivity</td>
<td>Ω·cm</td>
<td>&gt;10¹⁴</td>
</tr>
<tr>
<td>Dielectric strength</td>
<td>kV/cm</td>
<td>900</td>
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<tr>
<td>Dielectric constant</td>
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<td>2.30</td>
</tr>
<tr>
<td>Dissipation factor, tan δ</td>
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</tr>
<tr>
<td>at 50 Hz</td>
<td></td>
<td>0.00019</td>
</tr>
<tr>
<td>at 1 kHz</td>
<td></td>
<td>0.0005</td>
</tr>
<tr>
<td>at 0.1 MHz</td>
<td></td>
<td>0.00025</td>
</tr>
</tbody>
</table>
3.2 Blend and sample preparation

MBM was sieved using meshes with the pore size of 600 micron and 300 micron and dried 24h at temperature 50\(^\circ\)C. Blends of MBM and UHMWPE were obtained by mixing the two components with a mechanical shaker. Blends of meat and bone meal (MBM) and UHMWPE were prepared in the ratios of: (1) 10% MBM, 90% UHMWPE; (2) 20% MBM, 80% UHMWPE; (3) 30% MBM, 70% UHMWPE; (4) 40% MBM, 60% UHMWPE; (5) 50% MBM, 50% UHMWPE.

Plastics samples were obtained by compression molding of the mixture at a temperature of 180\(^\circ\)C, a pressure of 20 MPa for 5 minutes and cooled to 70\(^\circ\)C under pressure. Figure 3.3 shows MBM powder as received and after sieving. Molds and plungers and compression molding machine used to produce the plastics samples are shown in Figure 3.4. Dog bone shaped samples used for mechanical analysis (ASTM D638-86) are shown in Figure 3.5.

**Figure 3.3:** As-received” (left) and sieved (right) MBM.
Figure 3.4: Molds and plungers (left), compression molding machine (right).

Figure 3.5: Dog bone shaped samples.
3.3 Principal experimental and characterization techniques:

3.3.1 Thermal analysis

Differential scanning calorimetry (DSC; Model 2920 TA instruments) at a heating rate of 20°C min\(^{-1}\) was carried out to determine the denaturing temperature (\(T_d\)), degree of crystallinity (\(T_g\)) and the safe processing window for the protein material. Thermogravimetric analysis (TGA) was carried out under Nitrogen purge (40mL min\(^{-1}\)) at a heating rate of 20°C min\(^{-1}\) with TA instruments Hi Res TGA 2950 to study thermal stability. The total crystallinity of the samples was characterized as a ratio of the heat of fusion for UHMWPE in a sample to that of 100% crystalline polymer.

3.3.2 Mechanical properties

Tensile stress at break, Young’s modulus and % of elongation were measured using the Instron testing machine (Model 1125). The test was performed under controlled environment (20°C, 65% RH) according to the standard test method for tensile properties of plastics (ASTM D638 – 86) at 5 mm min\(^{-1}\) cross head speed with a static load cell of 100 kN.

3.3.3 Moisture testing

A Sartorius moisture analyzer was used to analyze the moisture content of the blends. Moisture content was determined by Equation 3.1

\[
MC = \left( \frac{W_o - W_{od}}{W_o} \right) \times 100
\]  

(3.1)

where \(MC\) is moisture content, \(W_o\) the initial and \(W_{od}\) is the final weight after drying.

3.4 References:

CHAPTER 4

BIODEGRADABLE PLASTICS FROM BLENDS OF DENATURED NON DEFATTED MBM and UHMWPE.

4.1 Introduction

The outbreak of Bovine Spongiform Encephalopathy (BSE) has led to the restriction/prohibition of the use of various animal co-product proteins in the U.S and the European Union as an ingredient in ruminant feed [1]. This has forced rendering industries, which recycle the animal co-products into invaluable ingredients such as protein meal and fats for animal feed, to explore various alternative uses, such as biofuels and bioplastics.

Plant proteins and animal proteins are two abundantly available sources that can serve as a biodegradable alternative to the petroleum polymers. Biodegradable plastics can be reduced to single compounds in the natural environment by microorganisms, which are less harmful to the environment. Whey protein, soy protein, egg white are just some of available proteins which are being used for biodegradable film and plastic making [2]. Feathermeal and bloodmeal proteins produced by animal co-product industry are also being studied for use as biodegradable plastics [3, 4].

It is necessary to highlight that proteins are exceptionally versatile materials and their industrial applications for fabrication of plastics are considered very seriously. Their primary source is not depletable, and they can be obtained with a wide variety of possible properties needed for a specific application.
For instance, soy protein has been studied intensively as an alternative to petroleum derived polymers in the manufacture of plastics reinforced with natural fibers (pineapple leaf, flax and ramie) [5]. Natural plant-derived fibers, such as wood, hemp, flax, jute and the like open up new important way to produce the biodegradable materials. Natural fibers/synthetic polymer composites are already attracting significant attention as an alternate to conventional building and automotive materials [6]. Lightweight, strong, and low-cost bio-fibers are poised to replace glass and mineral fillers in numerous applications.

Studies have shown that plastics and polymer blends from protein exhibit acceptable strength and improved biodegradability. Proteins are readily available from numerous sources and can be readily tailored to fit specific applications. This research focuses on animal protein meat and bone meal (MBM) plastics and blends since they are abundant due to the current outbreak of Bovine Spongiform Encephalopathy (BSE) also know as “mad cow disease”.

Besides, mechanical properties this research focuses on investigating thermal properties of the fabricated plastics and their potential applications. For example we produced flower pots made of MBM plastics (Figure 4.1).

Figure 4.1: MBM flower pots.
4.2 Meat and bone meal (MBM):

MBM is a dry and rendered product from mammal tissues which usually contains 50% protein, 9.5% fat, 10.1% calcium, and 4.8% phosphorus. It was mostly used for animal feeding because of high protein content. For example, it may be added to the cow food up to 5% [7]. Considering MBM for other applications has become an important topic for rendering industry since the emergence of bovine spongiform encephalopathy (1986). For instance, European Union (EU) has banned the use of all processed mammalian proteins in feeds for farm animals since January 2001 [8].

In the USA, MBM can be still used for feeding non-ruminant animals (pigs, fish, poultry, and household pets). However, more strict restrictions in the nearest future are inevitable. In general around 50% of a slaughtered animal cannot be consumed by human, so it should be recycled. According to the United State Department of Agriculture 2002 Report 35.7 million cattle, 100 million pigs and nearly 9 billion chickens and turkeys were slaughtered in the U.S and consequently 9.2 billion pounds of protein meals are produced (MBM has the highest volume). In case of prohibition of using MBM in the animal feeding, it will have to be land filled or incinerated [8], which will affect the rendering industry severely. Therefore, investigations are ongoing about using MBM as an alternative fuel [9], sand replacement in cement based materials [10], fertilizers, adhesive for poly-wood industry [11].

4.3 Materials

Same as those presented in Chapter 3.
4.4 Results and Discussion

4.4.1 Thermogravimetric and differential scanning calorimetry analysis

The TGA and DSC curves obtained for non defatted MBM powder, plastic and UHMWPE are presented in Figure 4.2 (TGA), Figure 4.3 (DSC neat MBM and UHMWPE powders) and Figure 4.4 (DSC of MBM/UHMWPE blends).

Figure 4.2 shows that for non-defatted MBM powder initial weight loss was evident above 100°C. This result could be attributed to water loss. Further degradation was evident at 265°C and this can be attributed to the peptide bond breakage within the protein. Finally, higher temperatures lead to the total degradation.

Figure 4.2: Thermal analysis (TGA) of non defatted MBM powder and plastics samples produced at a temperature of 180°C, a pressure of 20 MPa for 5 minutes and cooled to 70°C under pressure.
DSC data (Figure 4.3 (a)) shows a $T_g$ of about $50^\circ$C for the MBM powder.

Figure 4.3 (a) also indicates the presence of denaturation (unfolding) temperature ($T_d \sim 134^\circ$C). Thus, the protein was not fully denatured during the rendering process, and further protein unfolding took place upon the heating. Figure 4.3 (b) shows that UHMWPE powder melted at $\sim 140^\circ$C.

![Graph showing DSC data for MBM and UHMWPE](image)

**Figure 4.3:** DSC thermographs MBM and UHMWPE (powder) (a) MBM;
(b) UHMWPE.
It can be observed from Figure 4.4 that in plastics made of UHMWPE/MBM blend two endothermic peaks occurred. The first peak at $\sim 130-135^\circ C$ and the other at the melting temperature of pure UHMWPE ($\sim 140^\circ C$). These peaks can be attributed to presence of different types of UHMWPE crystals. We suggest that the lower peak is associated with an interaction between UHMWPE and MBM fat. No other thermal transitions were evident at temperatures below $200^\circ C$.

**Figure 4.4:** DSC thermographs UHMWPE and MBM/UHMWPE blends. All samples were molded at a temperature of $180^\circ C$, a pressure of 20 MPa for 5 minutes and cooled to $70^\circ C$ under pressure.
The melting depression occurred within the blends indicating some interaction between materials in the blend. The data in Table 4.1 shows that the crystallinity of UHMWPE in blends was not greatly affected with increase in MBM content. The introduction of MBM into the UHMWPE matrix at 10% MBM resulted into reduction of the regular packing of UHMWPE chains, leading to lower crystallinity in comparison with pure UHMWPE. Interestingly, at higher MBM content there was increase in crystallinity.

Table 4.1: Peak temperature and enthalpy of melting for UHMWPE and MBM/UHMWPE blends.

<table>
<thead>
<tr>
<th>UHMWPE content of blend, (% Wt)</th>
<th>Peak temperature (Lowest T)° C</th>
<th>H_m (J/g)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE (Powder)</td>
<td>142.81</td>
<td>154.4</td>
<td>55</td>
</tr>
<tr>
<td>UHMWPE (Plastic)</td>
<td>135.18</td>
<td>135.0</td>
<td>48</td>
</tr>
<tr>
<td>MBM/UHMWPE(10/90)</td>
<td>134.07</td>
<td>119.0</td>
<td>42.3</td>
</tr>
<tr>
<td>MBM/UHMWPE(20/80)</td>
<td>133.59</td>
<td>121.63</td>
<td>43.3</td>
</tr>
<tr>
<td>MBM/UHMWPE(30/70)</td>
<td>132.71</td>
<td>125.88</td>
<td>44.8</td>
</tr>
<tr>
<td>MBM/UHMWPE(40/60)</td>
<td>133.05</td>
<td>144.0</td>
<td>51.2</td>
</tr>
<tr>
<td>MBM/UHMWPE(50/50)</td>
<td>132.13</td>
<td>156.02</td>
<td>55.5</td>
</tr>
</tbody>
</table>
4.4.2 Tensile testing analysis

Mechanical properties obtained from tensile measurements for the compression molded samples are presented in Figures 4.5, 4.6 and 4.7. UHMWPE is a ductile semi crystalline polymer with high elongation at break and a medium tensile (Young’s) modulus. Tensile strength and % elongation are observed to decrease with increasing MBM content.

The mechanical properties of protein based materials can partly be related to the distribution and intensity of inter–and intra molecular interactions. The mechanical properties elongation and strength, of protein plastics are substantially lower than synthetic materials (Table 4.2).

Table 4.2: Mechanical properties of non-denatured and denatured protein plastics, and commercial petroleum based plastics.

<table>
<thead>
<tr>
<th>Plastics</th>
<th>Elongation %</th>
<th>Modulus (GPa)</th>
<th>Tensile Stress at Max Load (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-defatted MBM Plastics</td>
<td>1.2</td>
<td>2.59</td>
<td>6.97</td>
</tr>
<tr>
<td>Defatted MBM Plastics</td>
<td>1.6</td>
<td>2.92</td>
<td>12.67</td>
</tr>
<tr>
<td>Blood meal Plastics</td>
<td>1.6</td>
<td>4.7</td>
<td>16</td>
</tr>
<tr>
<td>Feather meal</td>
<td>1.4</td>
<td>4.9</td>
<td>13.2</td>
</tr>
<tr>
<td>Soybean</td>
<td>2.6</td>
<td>1.6</td>
<td>35</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>60-120</td>
<td>2.4</td>
<td>55-69</td>
</tr>
<tr>
<td>Polymethyl- methacrylate</td>
<td>2.0-10</td>
<td>2.4-2.8</td>
<td>48-69</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>1-2.5</td>
<td>2.8-3.5</td>
<td>24-38</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>350-450</td>
<td>1.050</td>
<td>20-22</td>
</tr>
</tbody>
</table>
Figure 4.5 shows that the tensile (Young’s) modulus decreases with increase in MBM content up to 30% and increases at 40, 50 and 100% concentrations of MBM deviating from the mixing rule in a negative manner. This phenomenon could be due to low interfacial adhesion between UHMWPE and MBM phases.

Figure 4.6 demonstrates that tensile strength at break decreased with increase in MBM content. The maximum elongation at break occurs for the blend of 10/90 MBM/UHMWPE indicating, however, that even low MBM concentration contribute negatively to the extension of the material, if compared with the neat UHMWPE (Figure 4.7).

Both tensile strength and elongation at break properties can be seen to decrease significantly with increase of MBM content. This reduction observed might be due to poor interfacial adhesion between MBM and UHMWPE phases, which causes poor stress-transfer between the matrix and the dispersed phase.
**Figure 4.5:** Tensile (Young’s) modulus of MBM, UHMWPE and MBM/UHMWPE blends. Samples were molded at a temperature of 180°C, a pressure of 20 MPa for 5 minutes and cooled to 70°C under pressure.

**Figure 4.6:** Tensile strength at break MBM, UHMWPE and MBM/UHMWPE blends. Samples were molded at a temperature of 180°C, a pressure of 20 MPa for 5 minutes and cooled to 70°C under pressure.
Figure 4.7: % Elongation at break MBM, UHMWPE and MBM/UHMWPE blends.

Samples were molded at a temperature of 180°C, a pressure of 20 MPa for 5 minutes and cooled to 70°C under pressure.
4.5 Modeling of mechanical properties of plastics from MBM/UHMWPE blends

The mechanical properties of two phase composites/blends consisting of a continuous polymer phase and a dispersed phase have been greatly studied and as a result several models are available to describe the modulus, tensile strength and elongation at break as a function of the inclusion volume.

Figure 4.8 shows again that the stiffness of the blended plastics depends on the ratio between UHMWPE and MBM in blend. Even with the increase of (stiffer) MBM component the elastic modulus initially decreases.

For polymer blends containing particles of any modulus, Kerner equation has been used to model the level of stiffness. The well established equation, which considers the dispersed phase as spheroidal in shape, the system as isotropic and the adhesion between the two phases is perfect, takes the following form [3, 12-18].

\[
E = E_1 \frac{\phi_2 E_2}{(7 - 5\nu_1)E_1 + (8 - 10\nu_1)E_2} + \phi_1 \frac{15(1 - \nu_1)}{\phi_1(7 - 5\nu_1)E_1 + (8 - 10\nu_1)E_2 + 15(1 - \nu_1)}
\]  

(4.1)

where \( E, E_1, E_2 \) are the moduli for the binary blend, the matrix and the dispersed phase, respectively; \( \phi_1, \phi_2 \) volume fractions of the matrix and dispersed phase respectively; \( \nu_1 \) represents the Poisson ratio for the matrix (to estimate the volume fractions the density of MBM was calculated to be 1.27 g/cm\(^3\)).
Equation 4.1 is valid for ideal stress transfer through the interface, indicating strong adhesion between the phases. If the stress transfer does not occur there is no adhesion between the phases and Kerner equation takes the simple form assuming $E_2$ to be zero. This is represented by Equation 4.2:

$$E = E_i \frac{(7 - 5\nu_1)\phi_i}{15(1-\nu_1)\phi_2 + (7 - 5\nu_1)\phi_i}$$  \hspace{1cm} (4.2)

Figure 4.8: Tensile modulus for MBM/UHMWPE blends and comparison with theoretical Kerner model at each volume fraction. Samples were molded at a temperature of 180\(^0\)C, a pressure 20 MPa for 5 min, followed by cooling to 70\(^0\)C under pressure.
Figure 4.8 shows that the theoretical prediction by Equations 4.1 and 4.2 indicate that there is a poor adhesion between UHMWPE and MBM phases. This may be explained due to difference in polarity (being MBM polar and UHMWPE non-polar material).

Nielsen developed a basic model that describes the elongation at break for a polymer composite material. For the case of perfect adhesion with the assumption that the matrix breaks at the same elongation in the composite as in neat polymer, the elongation at break is given by

\[
\varepsilon_c = \varepsilon_m \left( 1 - \phi^{1/3} \right) \tag{4.3}
\]

where \(\varepsilon_c\) is the elongation to break of the blend, \(\varepsilon_m\) is the elongation at break of polymer constituting the matrix and \(\phi\) is the volume fraction of the filler.

Figure 4.9 shows the change in elongation (or % tensile strain at break) for the MBM/UHMWPE blends. There is a clear negative deviation from the mixing additive rule. The elongation at break was observed to decrease gradually with increase in filler volume fraction. The decrease in elongation at break in the polymer blend is due to the fact that the deformation of the filler is much less than that of the polymer matrix: thus the filler forces the polymer matrix to deform more than the overall deformation of the composite.

There is a clear indication of poor adhesion between UHMWPE and MBM (Figure 4.9), as the experimental points are below the elongation values predicted by Equation 4.3.
Figure 4.9: % elongation at break for MBM/UHMWPE blends and comparison with Nielsen theoretical modes at each volume fraction. Samples were molded at a temperature of 180°C, a pressure 20 MPa for 5 min, followed by cooling to 70°C under pressure.

Figure 4.10 shows the tensile strength results for MBM/UHMWPE blends. The presence of dispersed phase (filler) is often expected to decrease the tensile strength of the matrix material. Nicolas and Narkis proposed that the area fraction depends on the volume fractions to two thirds power [19].

\[
\sigma = \sigma_m \left(1 - K\phi^{2/3}\right)
\]  

(4.4)

(K=1.21 for spherical fillers if there is no adhesion and if fracture goes through the filler-matrix interface)
where $\sigma_c$ is the composite tensile strength, $\sigma_m$ is the polymer matrix tensile strength and $K$ is a constant, and $\phi$ is the volume fraction of the filler. The values of the stress at break are significantly below those predicted by Equation 4.4. The results once again indicate there is a low interaction between the components in the blend.

**Figure 4.10:** Tensile strength at break for MBM/UHMWPE blends and comparison with Nicolas-Narkis theoretical model at each volume fraction. Samples were molded at a temperature of $180^\circ$C, a pressure 20 MPa for 5 min, followed by cooling to $70^\circ$C under pressure.
4.6 Conclusions

This study confirms that the newly developed protein-based plastic and its blends display a suitable range of mechanical, thermal and degradation properties. This might eventually allow its use in the traditional application of plastics. For many applications it will be necessary to enhance the mechanical properties by testing an influence a wide range of plasticizers, interfacial modifiers and additives materials on blends mechanical and biodegradation properties.

The results interpreted in terms of theoretical models to describe mechanical properties such as extensibility, tensile strength and stiffness of the plastics made from MBM/UHMWPE blends at various volume ratio. The properties of the MBM/UHMWPE blends negatively deviated from the mixing rule.

From thermal analysis it was evident that there was an interaction between the components. This was evident from melting depression occurrence

From modeling its mechanical properties: tensile strength, tensile modulus and % elongation it was evident that interface adhesion in the blends should be improved in order to achieve better mechanical properties.
4.7 References:


CHAPTER 5

BIODEGRADABLE PLASTICS FROM BLENDS OF DENATURED DEFATTED MBM and UHMWPE

5.1 Experimental

5.1.1 Materials

Materials used are the same as those in Chapter 3.

5.2 Preparation of defatted MBM

In order to remove fat from the MBM material, fatty content of MBM was dissolved and extracted by hexane, followed by drying to remove the residual solvent. Then, MBM material was sieved through meshes with the pore size of 600 micron and 300 micron. The sieved meat and bone meal powder’s moisture content was found to be ~7%. Higher moisture content than that of non-defatted MBM (~5 %) can be associated with the effect of fatty content removal and macroscopic characteristic of powder.

Photograph of as-received MBM powder and sieved defatted powder are shown in Figure 5.1. The sieved and fat extracted powder has a finely ground structure (less than 300 micron), less bone particles, and less hair. Thus plastic made with the defatted MBM powder should have better mechanical and physical properties.

![Figure 5.1: MBM “As-received” (left) and defatted (right)](image-url)
5.3 Principal experimental and characterization techniques:

The following techniques are addition to those listed in Chapter 3.

5.3.1 Morphology studies

The morphology of the polymer matrix has been reported to be affected by the distribution of dispersed phase [1]. To visualize internal morphology of the MBM/UHMWPE blends, the specimens were broken in liquid nitrogen. Then, the fractured surface was analyzed with optical microscope. It was found that the outer surface morphology was different from the cross sectional area.

5.3.2 Thermal and mechanical analysis

The modified rendering protein powders mixed with MBM material were compression molded to produce composites and plastic samples for evaluating various properties, such as tensile mechanical behaviors of the samples were thoroughly characterized according to ASTM standard D638-03. Specifically, mechanical properties were measured using DMA (dynamic mechanical analysis), and stress-strain testers (Instron). The ASTM standard D5026-06 was used for DMA instrument.

Stress-strain properties such as stress-at-break, modulus, and elongation were key parameters used to evaluate the performance of these plastics with different loading of MBM. DSC and TGA were utilized to detect temperature transitions and thermal stability of the plastic materials.
5.3.3 Contact angle measurements

The water contact angle measurements were performed using a water droplet placed on the surface of the material. Contact angle measurements were performed with Kruss DSA-10 apparatus. A water droplet was placed on the surface of the sample and the evolution of the droplet spreading was recorded. A CCD video camera and video analysis software were used to determine the contact angle. Figure 5.2 shows typical droplet shape.

![Figure 5.2](image_url) Water droplet on MBM/UHMWPE plastic.

**Figure 5.2**: Water droplet on MBM/UHMWPE plastic.
5.4 Results and discussion

5.4.1 Surface and cross-sectional morphology analysis

Figure 5.3 shows the microstructure images produced by optical microscope of the surface (20X on left side) and fractured cross sectional area (45X on right side) of MBM/UHMWPE blends. It was evident that the outer surface was smooth with relative low fluctuation and the inner of the plastic sample had higher fluctuations. It is clear that MBM particles form agglomerates

The boundaries of the MBM domains are completely smooth, and there are no signs of adhesion of UHMWPE matrix to the domains. For (Figure 5.3 (f)) 50-50 composition, the morphology appears to be co-continuous as the concentration approaches phase inversion region. It is not clear which phase forms the matrix and which the dispersed phase is. For (Figure 5.3 d, and e) 30-70 and 40-60 compositions the UHMWPE phase can be distinguished. However, the adhesion between the two phases appears weak.
Figure 5.3: Micrographs of surface (on the left (X20)) and cross sections (on the right (X45)) of (a) MBM. (b) MBM/UHMWPE (10/90), (c) MBM/UHMWPE (20/80), (d) MBM/UHMWPE (30/70), (e) MBM/UHMWPE (40/60), (f) MBM/UHMWPE (50/50).
5.4.2 Plastics from MBM thermogravimetric and differential calorimetry analysis

Defatted MBM powder, which contained approximately 7-9% moisture, was analyzed using DSC and TGA to determine its thermal stability. Results of thermal analysis of the virgin materials (MBM and UHMWPE) using differential scanning calorimetry (DSC) and TGA (Thermo gravimetric analysis) are shown in Figures 5.4 and 5.5, respectively.

The TGA thermographs in Figure 5.4 (a, b) show degradation temperature measured for MBM powder and plastic (230°C). There is an initial weight loss that occurs in the MBM at 100°C, and is mainly due to water evaporation from the sample. UHWMPE degradation temperature was found to be 410°C.

Even though the MBM was thermally treated via the rendering process DSC data in Figure 5.5 indicated the presence of denaturing at 150°C. Thus indicating that the protein was not fully denatured during the rendering process.

Having determined denaturation and degradation temperatures of both components compression molding parameters were established: molding temperature of 180°C, time 5 minutes and pressure 20 MPa. Samples were cooled in the mold up to ≤ 70°C under pressure on hot press (Carver 60 Ton Economy Motorized press). Flash was removed by sanding down the edges of the specimen with abrasive sandpaper.
Figure 5.4: TGA of defatted MBM and UHMWPE (a) MBM.; (b) UHMWPE
DSC thermographs Figure 5.5 (a) shows that MBM has a $T_g$ (glass transition temperature) at 50°C while molded MBM plastic $T_g$ was at 70°C. This may be attributed to better packing of MBM in plastic form, but the onset of degradation for both powder and plastic remained at 230°C. UHMWPE DSC thermograph (Figure 5.5 (b)) shows that UHMWPE melting temperature occurred at ~140°C for powder and at ~135°C for plastic. No other transitions were evident. The polymer is highly crystalline (55%).
Figure 5.5: DSC thermographs for defatted MBM and UHMWPE (powder)

(a) MBM; (b) UHMWPE
5.4.3 DSC analysis of the blends

The thermal behavior of the blend samples was measured using DSC. The sample chamber was purged with nitrogen; Samples of about 6 mg were equilibrated at 25°C, heated at a rate of $10 \, ^\circ C / \text{Min}$ up to 200°C. The DSC analysis (Figure 5.6) indicates that there is change in melting UHMWPE temperature for each of the blend ratios.

![DSC thermographs for MBM/UHMWPE blends. All samples were molded at a temperature of 180°C, a pressure of 20 MPa for 5 minutes and cooled to 70°C under pressure.](image)

**Figure 5.6:** DSC thermographs for MBM/UHMWPE blends. All samples were molded at a temperature of 180°C, a pressure of 20 MPa for 5 minutes and cooled to 70°C under pressure.
The values of heat of crystallization and heat of fusion were calculated per gram of UHMWPE in sample [2, 3]. Table 5.1 shows the peak temperatures of the blends and heat to melt per gram for UHMWPE. % of crystallinity of the blends was not influenced by MBM content.

**Table 5.1: Peak temperature and enthalpy UHMWPE and MBM/UHMWPE blends**

<table>
<thead>
<tr>
<th>UHMWPE content of blend,( % Wt)</th>
<th>Peak melting temperature ⁰C</th>
<th>$H_m$ (J/g)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE Plastic</td>
<td>135.18</td>
<td>135.0</td>
<td>48</td>
</tr>
<tr>
<td>MBM/UHMWPE(10/90)</td>
<td>135.48</td>
<td>129.1</td>
<td>45.9</td>
</tr>
<tr>
<td>MBM/UHMWPE(20/80)</td>
<td>133.9</td>
<td>139.25</td>
<td>49.5</td>
</tr>
<tr>
<td>MBM/UHMWPE(30/70)</td>
<td>130.74</td>
<td>127.82</td>
<td>45.4</td>
</tr>
<tr>
<td>MBM/UHMWPE(40/60)</td>
<td>131.98</td>
<td>131.1</td>
<td>46.7</td>
</tr>
<tr>
<td>MBM/UHMWPE(50/50)</td>
<td>130.79</td>
<td>140.64</td>
<td>50.0</td>
</tr>
</tbody>
</table>

A certain melting point depression is evident from data in Table 5.1 with increased proportion of MBM in the blend. The results indicate that there is an interaction between UHMWPE and MBM material. Cortazar et al. [4] studies on melting depression of PEO (poly ether oxide) and PMMA (poly methyl-methacrylate) blends concluded that melting depression depended on blend compositions and the level of crystallinity and interaction between the components. Jonza et al. [5] also depicts that the source of melting depression is due to both morphological and thermodynamics of the components, Figure 5.7 [4, 5]. From the Table 5.1 it is conclusive that there is some interaction between UHMWPE and MBM material.
Figure 5.7: Sketch depicting (A) morphological and (B) thermodynamic melting point depression. Note the equation given in the figure for thermodynamic $T_{m}$ depression assumes infinite molecular weight of each component of the binary blend [5]. According to Hoffman and Weeks the equilibrium melting temperature of the polymer $T_{m}^{0}$ is defined as the melting point of an assembly of crystals, $\gamma$ represents the thickness ratio between the initial thickness of chain folded lamella and the final lamella thickness, $T_{c}$ is the isothermal crystallization. To determine $T_{m}^{0}$ a plot of $T_{c}$ versus $T_{m}$ is prepared and a line is drawn where $T_{m} = T_{c}$. The experimental data are extrapolated to the intersection with the line. The temperature of intersection is $T_{m}^{0}$ [6, 7]. Nishi-Wang equation is for melting depression is associated with mixing crystalline and amorphous polymer. $T_{mb}^{0}$ is the melting point of semi crystalline polymer in the mixture,
\( T_m^0 \) is the melting point of the pure semi crystalline polymer, \( R \)-gas constant, \( V \) is the molar volume fraction, \( \Delta H_f \)-enthalpy of fusion per mole of the repeating unit, \( \chi \) is Flory-Huggins polymer to polymer interaction parameter and \( \phi \) is the volume fraction of the non-crystalizable component [6-8].

5.4.4 Tensile testing analysis

The mechanical properties of the blended plastics containing defatted MBM showed significant improvement when compared with non-defatted MBM (Figures 5.8, 5.9 and 5.10). In general addition of UHMWPE to the defatted MBM improved elongation at break and the stress at break of the plastics. 10% blend of MBM and UHMWPE showed the highest breaking stress and % elongation 21.52 MPa, and 32.9% respectively. The highest modulus was demonstrated by 30% blend.

The variation of tensile strength and elongation at break of MBM/UHMWPE blends with increase in MBM content are shown in Figures 5.8 and 5.10. It can be seen that both properties significantly decrease with increase in MBM content. The reduction observed might be attributed to poor interfacial adhesion between MBM and UHMWPE phases, which causes poor stress-transfer between the matrix and the dispersed phase.

Figure 5.9 shows the effect of MBM content on Young’s modulus of MBM/UHMWPE blends. It shows an increase to a maximum of 30% of defatted MBM content. However further increase in MBM content led to decrease in Young’s modulus. This characteristic stiffness arises as MBM tend to agglomerate within UHMWPE matrix at higher contents.
Figure 5.8: Tensile strength of MBM and MBM/UHMWPE blends. All samples were molded at a temperature of 180°C, a pressure of 20 MPa for 5 minutes and cooled to 70°C under pressure.

Figure 5.9: Tensile modulus of MBM and MBM/UHMWPE blends. All samples were molded at a temperature of 180°C, a pressure of 20 MPa for 5 minutes and cooled to 70°C under pressure.
**Figure 5.10:** % Elongation MBM and MBM/UHMWPE blends. All samples were molded at a temperature of 180°C, a pressure of 20 MPa for 5 minutes and cooled to 70°C under pressure.
### 5.4.5 Dynamic mechanical analysis

From dynamic mechanical analysis storage modulus was determined for the blends under consideration. Even so blend storage modulus was lower compared to neat MBM. However, MBM storage modulus decreased drastically with increase in temperature. Storage modulus improved for all of the blends but with increase in MBM content storage modulus varied with content, **Figure 5.11** (a) Loss modulus and tan delta also increased with increase in MBM content **Figure 5.11** (b).

**Figure 5.12** shows that 50% MBM/UHMWPE blend exhibited improved dampening (height of tan delta peak) compared to all other blends. These improved mechanical properties may be attributed to blend constitution and its ability to dissipate energy.
Figure 5.11: Dynamic mechanical properties of MBM and MBM/UHMWPE blends. All samples were molded at a temperature of 180°C, a pressure of 20MPa for 5 minutes and cooled to 70°C under pressure. (a) Storage modulus, (b) loss modulus.
Figure 5.12: Dynamic mechanical properties of MBM and MBM/UHMWPE blends. All samples were molded at a temperature of 180°C, a pressure of 20MPa for 5 minutes and cooled to 70°C under pressure
5.4.6 Contact angle analysis

The results of contact angle measurements are presented in Table 5.2. The material’s wettability is quantitatively illustrated by the obtained measurement of the contact angle after deposition of the water droplet over the surface of blend sample. For pure MBM water wet the surface well because of the hydrophilic nature of the material. But with increase in UHMWPE content the contact angle increases because of the polymer hydrophobic nature.

Table 5.2: Contact angle measurements of MBM/UHMWPE blends

<table>
<thead>
<tr>
<th>Blend %</th>
<th>Initial Value (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE</td>
<td>86</td>
</tr>
<tr>
<td>10% MBM</td>
<td>81</td>
</tr>
<tr>
<td>20% MBM</td>
<td>77</td>
</tr>
<tr>
<td>30% MBM</td>
<td>70</td>
</tr>
<tr>
<td>40% MBM</td>
<td>67</td>
</tr>
<tr>
<td>50% MBM</td>
<td>58</td>
</tr>
<tr>
<td>100% MBM</td>
<td>27</td>
</tr>
</tbody>
</table>

In conclusion the presence of MBM on the surface of the samples indicates that the samples may be biodegradable, since MBM is not fully screened by UHMWPE.
5.5 Modeling of mechanical properties of plastics from blends

Mechanical properties were modeled per theories presented in Chapter 3 to evaluate the difference between defatted and no defatted blends properties. Figure 5.13 (a) shows that the theoretical prediction by Equation 4.1 and 4.2 indicate intermediate to poor adhesion between the MBM and UHMWPE phases. This may be explained by the phase separation occurrence that was evident under the microscope Figure 5.3. Also, stiffness of the blended plastics depends on the ratio between the MBM and UHMWPE in the blend. With increase in the stiffer (MBM) component, the storage modulus of the plastic increases. The dependence deviates from the “mixing”, additive rule in a negative way. Storage modulus (Figure 5.13 a, b) was found to decrease with increase in temperature. In general, the data indicate that removal of fat from MBM somewhat improves the adhesion between the phases in the blend.
Figure 5.13: Tensile modulus (a) and storage modulus at 75°C (b) and (c) 25°C of MBM/UHMWPE blends and comparison with Kerner theoretical model at each volume fraction. Samples were molded at a temperature of 180°C, a pressure 20 MPa for 5 min, followed by cooling to 70°C under pressure.
Figure 5.14 shows the change in % elongation for MBM/UHMWPE blends. There is clear negative deviation from the mixing rule. The data was compared to Nielsen’s equation for perfect adhesion, Equation 4.3. The experimental data from Figure 5.14 clearly indicate poor adhesion between MBM and UHMWPE blends.

Figure 5.14: % Elongation at break for MBM/UHMWPE blends and comparison with Nielsen theoretical model at each volume fraction. Samples were molded at a temperature of 180°C, a pressure 20 MPa for 5 min, followed by cooling to 70°C under pressure.
Figure 5.15 shows that tensile strength for the blends of MBM/UHMWPE. The experimental values lie above those predicted by Equation 4.4, the results indicating some level of adhesion between the components of the blend.

Figure 5.15: Tensile strength for MBM/UHMWPE blends and comparison with Nicolas-Narkis theoretical model at each volume fraction. Samples were molded at a temperature of 180°C, a pressure 20 MPa for 5 min, followed by cooling to 70°C under pressure.
5.6 Water absorption

Figure 5.16 shows the water absorption by MBM/UHMWPE blends after different immersion times. Pure MBM absorbed the most water, the water absorption of MBM after a week was 50% and most water uptake occurred in the first few hours. 10% blend absorbed the least amount of water indicating that water absorption rate increased with increased MBM content. From the results obtained it is conclusive that blending MBM with UHMWPE does not change the hydrophilic nature of MBM protein.

Figure 5.16: Water absorption by MBM/UHMWPE blends as a function of time.

Samples were molded at a temperature of 180°C, a pressure 20 MPa for 5 min, followed by cooling to 70°C under pressure.
5.6.1 Mechanical properties of water immersed blends

The MBM/UHMWPE blends immersed in water were dried at 50\(^0\)C overnight and their mechanical properties were analyzed to determine the effect of water intake and drying on blends mechanical properties. Figure 5.17 that show the percentage weight change after the samples were dried.

The dried blends did not lose any other component apart from the water absorbed during water immersion test. Figure 5.18 shows that there was significant decrease in tensile stress in 10\%-50\% MBM/UHMWPE. Modulus and \% elongation also decreased for all blends but increased for 50\% blend after drying.

![Graph showing percentage weight changes of MBM/UHMWPE blends. Final dry weight subtracted from initial weight. Samples were molded at a temperature of 180\(^0\)C, a pressure 20 MPa for 5 min, followed by cooling to 70\(^0\)C under pressure.]

**Figure 5.17**: Percentage weight changes of MBM/UHMWPE blends. Final dry weight subtracted from initial weight. Samples were molded at a temperature of 180\(^0\)C, a pressure 20 MPa for 5 min, followed by cooling to 70\(^0\)C under pressure.
Figure 5.18: (a) Tensile strength (MPa), (b) Tensile modulus (GPa) and (c) % Elongation at break MBM/UHMWPE blends after drying. Samples were molded at a temperature of 180°C, a pressure of 20MPa for 5 minutes and cooled to 70°C under pressure.
5.7 Conclusions

Plastic samples from defatted MBM were successfully produced through compression molding process. These plastics exhibited comparable modulus and low strength and elongation than convectional plastics such as polystyrene. Plastics blends exhibited improved mechanical properties (beside stiffness) as compared to neat MBM plastics. Extension, tensile strength and stiffness results from mechanical analysis at various volume fractions were compared to existing theoretical models and showed better interface adhesion than in the non-defatted material.

MBM Young’s modulus comparison to theoretical model indicated that poor adhesion was still evident. Compatibilizers should be incorporated in the blends to improve adhesion properties. Overall, MBM material showed potential in development of polymer blends with synthetic polymers.
5.8 References:


CHAPTER 6
SUMMARY AND CONCLUSIONS

We have successfully developed compression molded biodegradable plastic formulations from blends of MBM and ultra high molecular weight polyethylene (UHMWPE). The results show that there is immense potential for designing and engineering eco friendly bio based materials from MBM.

The ratio of between the blend components, melt processing temperature and pressure affected the resulting properties of the biodegradable polymer blends. Among the different blends tested 30% blend demonstrated the best overall results under the present experimental conditions.

Both tensile strength and elongation at break properties decreased significantly with increase of MBM content. The reduction observed might be due to poor interfacial adhesion between MBM and UHMWPE phases.

In general MBM/UHMWPE blends modulus compared to existing theoretical models indicated that poor adhesion was evident in the blends.

Thermal properties analysis indicated that MBM/UHMWPE blends were thermally stable to be processed into viable plastics. MBM degradation temperatures at 265°C and 230°C for non defatted and defatted, respectively; and UHMWPE degradation temperatures at 410°C provide a large processing window which is highly desirable in the industry.
The morphology of the blends was found to change with increase in MBM content and phase separation in the blend was evident. Contact angle measurements showed that the blending of MBM with UHMWPE decreases the hydrophilic nature of MBM and thus decreasing the rate of part disintegration due to moisture intake hence creating a longer shelf life of the blend.

Water absorption after sample immersion in water was found to decrease with decrease in MBM content. After drying the water immersed samples it was evident that the structural integrity of the sample was retained since no other by product of the sample was lost apart from the water gained. Mechanical properties of samples immersed in water were however, found to have a decline in tensile strength and elongation were greatly influenced by the water intake indicating that water would drastically affect mechanical properties of the samples. Hence moisture intake should be controlled, if these materials were to be used in moisture or water conditions.

Defatting of the MBM with hexane was found to improve the mechanical properties of the resulting samples and it was conclusive that fat content interfered with the fabrication process.
CHAPTER 7

RECOMMENDATIONS AND FUTURE WORK

The mechanical properties of blends are largely influenced by the amino acid sequence of the polypeptide chains. In our opinion extrusion processing technique with use of plasticizers such as glycerol and chemical additives such as sodium sulfite and sodium dodecyl sulphite may lead to structural rearrangements and new improved interactions. Increased molecular interactions will result in a material that has higher tensile strength and stiffness.

Water absorption by the blends causing decrease in tensile strength, elongation and increased protein degradation can be reduced by the use of hydrophobic plasticizers that increases the rate of cross-linking which hence limits the extent of water absorption. MBM can be modified by binding hydrophobic plasticizers to the protein chains by acetylation reactions or during defatting of MBM with hexane.

Addition of suitable compatibilizers can reduce interfacial tension facilitate fine dispersion stabilize the morphology against destructive modification, and increase level of interfacial adhesion.

Impact testing analysis should be performed to study the blends toughness. Further optical analysis should be done to study the microtomic structure of cross sections of the blends.