

**FINAL REPORT**  
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*Biodegradable polymer blends and composites from proteins produced by animal co-product industry*

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**Collaborators:**

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**Duration of Project:** 12 months

## **Lay Summary:**

Most petroleum derived polymers are not biodegradable. This fact increases the waste disposal problem for commodity plastics and also the contamination of the environment. In addition to that, depleting of petrochemical resources necessitates producing biodegradable and economically feasible material. Biodegradable plastics can be reduced to single compounds in the natural environment by microorganisms, which are less harmful to the environment. Plant proteins and animal proteins are two abundantly available biodegradable sources that can serve as an alternative to the petroleum polymers. Feathermeal, blood meal and MBM (meat and bone meal) protein are being studied for use as biodegradable plastics, which are documented in our previous year's reports. Those have a potential in development of biodegradable items, such as flowerpots, golf tees, mulch film, and holding nails. However, further improvement of mechanical properties is needed. Properties can be improved by blending, formation of composites, or by using additives.

## **Objective**

The objective of this research was the development of biocomposite plastic out of MBM proteins blends with synthetic polymers. Specifically, we studied blends of MBM with polyethylene (PE) and determined that plastics, possessing good mechanical characteristics, can be prepared.

## **Project Overview:**

MBM protein was provided by Fats and Proteins Research Foundation (FPRF). In this particular term of our research, we employed MBM protein as reinforcement material for ultra high molecular weight polyethylene plastic, UHMWPE purchased from Sigma Aldrich in a powder form. MBM particle size was under 300micron. UHMWPE particle size and density range were 180 micron and 0.940g/cm<sup>3</sup> to 0.945g/cm<sup>3</sup> respectively. UHMWPE differs from conventional PE due to high degree of polymerization ranging from 100,000 to 250,000 g/mol. Thermal transition (DSC, TGA) measurement showed that UHMWPE is 55% crystalline and has 140 °C melting temperature and 410 °C degradation temperature.

Blends of defatted and non defatted 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%UHMW PE; (4) 40%MBM, 60% UHMWPE; (5) 50% MBM, 50%UHMWPE. All plastic were fabricated by compression molding at 180°C, 20 MPa for 5min.

Thermal transition and stability were determined with DCS (Differential scanning calorimetry) and TGA (Thermo gravimetric analysis). Mechanical properties were tested with Instron (stress-strain tester) and DMA (Dynamic mechanical analyzer). Water contact angle measurements were performed to analyze hydrophobicity of the plastic surface with respect to the MBM concentration. Result from the contact angle measurement can also be linked to morphology of plastic structure (how was each component distributed in structure during the plastic formation). In addition, morphology was analyzed with optical microscopy as well. Water absorption properties of the plastics were measured for one week period. Water intake is an important property of those plastic for their final application. All experimental results are given below.

From DCS experiment, the values of melting temperature and percentage of crystallinity for UHMWPE in blend with MBM were determined (**Table 1**). It can be concluded that a certain interaction occurs between UHMWPE and MBM powder during the plastic formation, since meting point depression were observed with increase of MBM content. However level of crystallinity and of blend was not influenced by MBM content which is not supporting conclusion driven with Tm depression fact. Further analysis is required for understanding the adhesion between components.

Tensile test experimental result showed that plastic made from blend of MBM and UHMWPE demonstrated improved mechanical properties comparing to plastic produced from pure defatted MBM (**Table 2**). DMA measurement showed that storage moduli (indication of stiffness) were found to be decreased with increase in temperature, which is common trend for plastics. Storage moduli were somewhat similar for the blends except for those with 1:1 (MBM:UHMWPE) ratio. We suggest that increase of storage modulus for the 1:1 plastic is due to the phase inversion at this concentration, where MBM phase become continuous. The same conclusion can be supported with loss factor ( $\tan \delta$ ) data obtained from DMA experiment. Plastics of 1:1 ratio showed higher  $\tan \delta$  value then plastics of other blend and pure HMWPE. (DMA graphs are not given).

**Table 1.** Melting temperature and crystallinity of UHMWPE in MBM blends.

UHMWPE content of blend with defatted MBM,(%w)	Peak melting temperature °C	Percent of crystallinity
UHMWPE	135.18	48
UHMWPE/MBM(90/10)	135.48	45.9
UHMWPE/MBM(80/20)	133.9	49.5
UHMWPE/MBM(70/30)	130.74	45.4
UHMWPE/MBM(60/40)	131.98	46.7

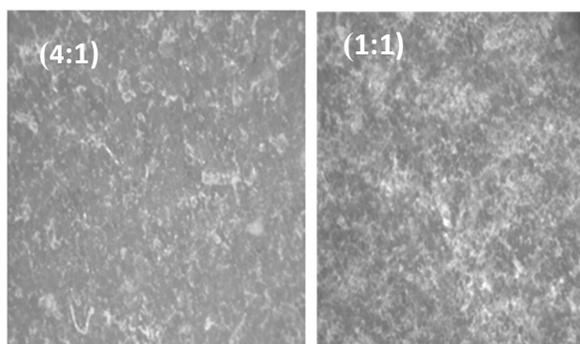
**Table 2.** Results of stress-strain experiments. Bold indicates results for blends with non-defatted MBM.

Blend composition	Stress at break (MPa)	Modulus (GPa)	Elongation at Break (%)
UHMWPE	28.56	1.25	441.5
10%	21.5/ <b>18.3</b>	0.74/ <b>0.48</b>	82 / <b>13.2</b>
20%	19.8/ <b>15.2</b>	0.81/ <b>0.45</b>	68.9/ <b>11</b>
30%	17.3/ <b>11.9</b>	0.85/ <b>0.34</b>	51.1/ <b>8.2</b>
40%	15.4/ <b>8.9</b>	0.81/ <b>0.49</b>	27.8/ <b>4.5</b>
50%	14/ <b>6.6</b>	0.75/ <b>0.53</b>	14.5/ <b>2.3</b>
100%	7.8	1.7	2.9

Decrease in water contact angle (**Table3**) was observed with increase of MBM content in the blend. This is due to the hydrophilic nature of MBM located at the surface. Results indicate that MBM distributed on surface evenly at each concentration. Optical microscope images show the outer surface of the blend samples (**Figure 1**). The surface was smooth with little fluctuations indicating that small MBM particles are placed at the outer part of the plastic. Images of sample's cross section (not given here) showed higher fluctuation at inner surface which supports that smaller MBM particles are placed at the outer region while larger particles are located inside the samples. **Figure 2** shows that pure MBM absorbed most water. 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 can be concluded that blending MBM with UHMWPE does not change the hydrophilic nature of MBM protein.

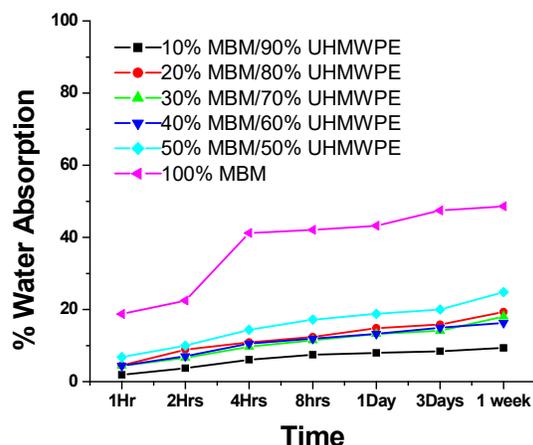
**Table 3.** Water Contact Angle measurements.

Blend composition %	Initial water contact angle (degree)
UHMWPE	86
10% MBM	81
20% MBM	77
30% MBM	57
40% MBM	67
50% MBM	58
100% MBM	27



**Figure1.** Surface morphology of UHMWPE/MBM blends (optical microscopy).

The UHMWPE/MBM blends immersed in water were dried at 50<sup>0</sup>C overnight and their mechanical properties were analyzed to determine the effect of water intake and drying on blends mechanical properties. The dried blends did not lose any other component apart from the water absorbed during water immersion. Change in mechanical properties (**Table 4**) with water absorption should be considered for final application of those blends.



**Figure2.** Water absorption by UHMWPE/MBM blends as a function of time.

**Table 4.** Results of stress-strain experiments for defatted MBM blends. Bold indicates results after water immersion.

Blend composition	Stress at break (MPa)	Modules (GPa)	Elongation at break (%)
UHMWPE	28.56	1.245	441.5
10%	21.52/ <b>17.86</b>	0.74/ <b>0.64</b>	82.3/ <b>25.8</b>
20%	19.79/ <b>12.68</b>	0.81/ <b>0.37</b>	68.9/ <b>31.2</b>
30%	17.31/ <b>10.47</b>	0.85/ <b>0.38</b>	51.1/ <b>21.8</b>
40%	15.4/ <b>9.45</b>	0.8/ <b>0.37</b>	27.8/ <b>22.9</b>
50%	13.96/ <b>7.90</b>	0.75/ <b>0.38</b>	14.5/ <b>16.7</b>
100%	7.76	1.7	2.9375

After studying the mechanical, thermal, and surface properties of two phase composites/blends consisting of a continuous polymer phase and a dispersed phase we focus on understanding the adhesion between components in blend and the effect of volume ratios on the mechanical properties. Models are available to describe the modulus, tensile strength and elongation at break as a function of the inclusion volume.

**Figure 3** shows that the stiffness of the blended plastics depends on the ratio between UHMWPE and non defatted 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.

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

where E, E<sub>1</sub>, E<sub>2</sub> 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 1.27g/cm<sup>3</sup>).

**Equation 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<sub>2</sub> to be zero. This is represented by **Equation 4.2**:

$$E = E_1 \frac{(7-5\nu_1)\phi_1}{15(1-\nu_1)\phi_2 + (7-5\nu_1)\phi_1} \quad (2)$$

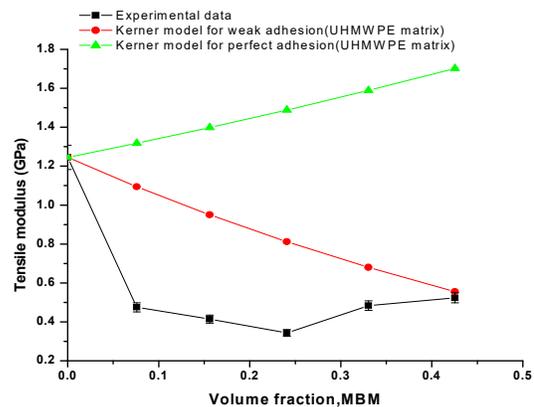
**Figure 3** shows that the theoretical prediction by **Equations 1** and **2** indicate that there is a poor adhesion between UHMWPE and MBM phases. This may be explained due to difference in polarity (being MBM polar and UHMWPE non-polar material).

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

$$\varepsilon_c = \varepsilon_m \left(1 - \phi^{1/3}\right) \quad (3)$$

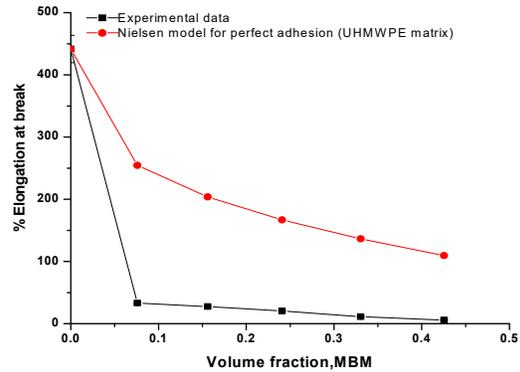
where  $\varepsilon_c$  is the elongation to break of the blend,  $\varepsilon_0$  is the elongation at break of polymer constituting the matrix and  $\phi$  is the volume fraction of the filler.

**Figure 3:** Tensile modulus for non defatted MBM/UHMWPE blends and comparison with theoretical Kerner model at each volume fraction.



**Figure 4** shows the change in elongation (or % tensile strain at break) for the UHMWPE/non-defatted MBM blend. 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**), as the experimental points are below the elongation values predicted by **Equation 3**.

**Figure 4:** % elongation at break for MBM/UHMWPE blends and comparison with Nielsen theoretical model at each volume fraction.

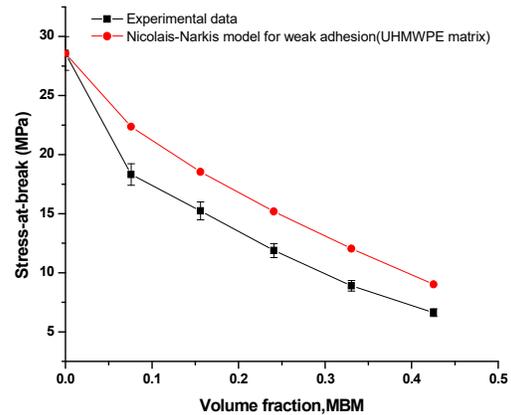


**Figure 5** shows the tensile strength results for MBM/UHMWPE blends. The presence of dispersed phase (filler) is often expected to decrease the tensile strength of the matrix material. Nicolas and Narkis proposed that the area fraction depends on the volume fractions to two thirds power:

$$\sigma = \sigma_m \left(1 - K\phi^{2/3}\right) \quad (4)$$

( $K=1.21$  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.

**Figure 5:** Tensile strength at break for MBM/UHMWPE blends and comparison with Nicolas-Narkis theoretical model at each volume fraction.

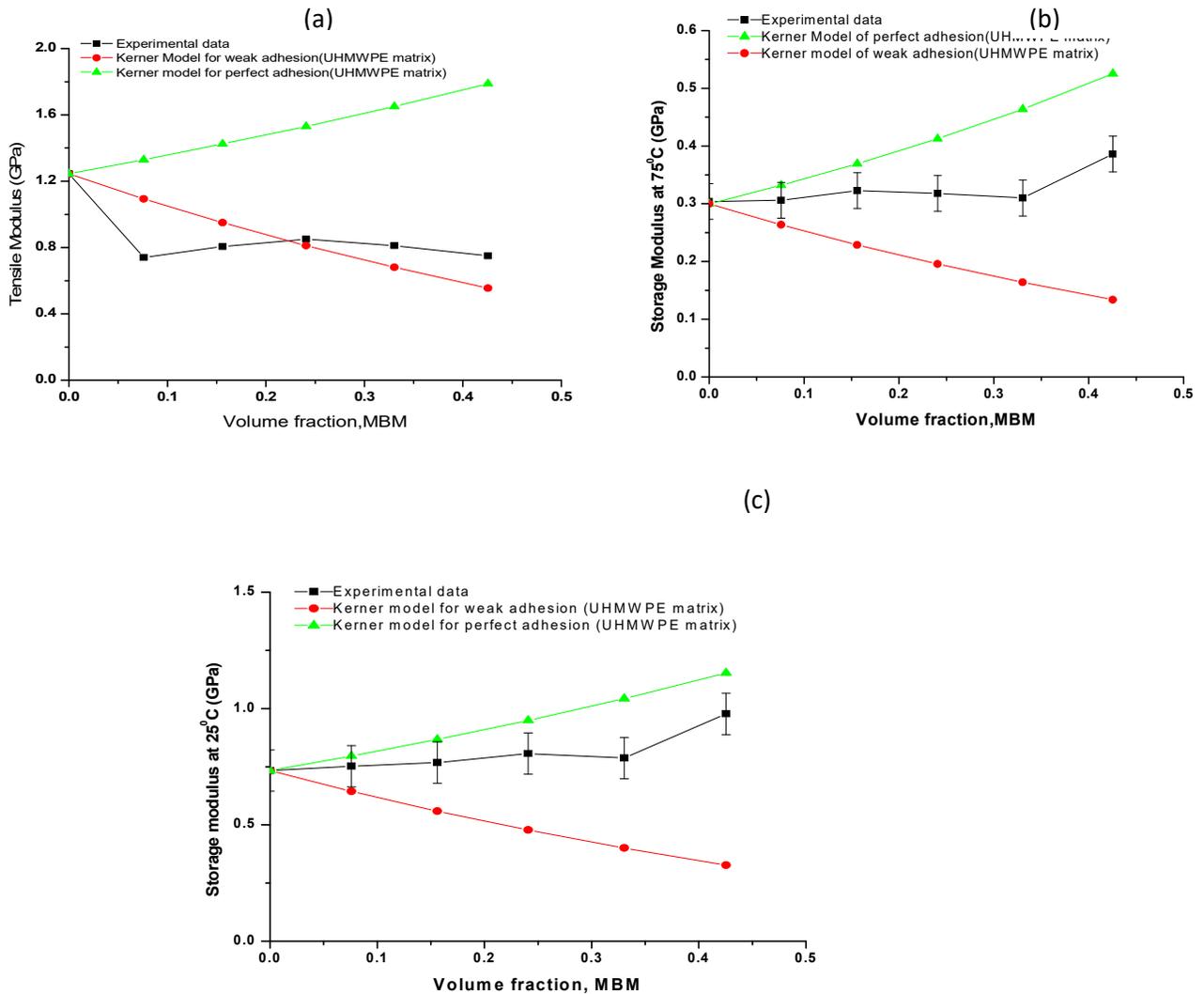


The values of the stress at break are significantly below those predicted by **Equation 4**. The results once again indicate there is a low interaction between the components in the blend.

While modeling mechanical properties of non defatted MBM containing blends indicate lower adhesion between components, modeling for defatted MBM containing blends show some level of adhesion. We use the same theories for modeling that we used for non defatted MBM/UHMWPE system. Models were applied to the storage and loss modulus besides tensile modulus. **Figure 6(a)** shows that the theoretical prediction by **Equation 1** and **2** indicate intermediate to poor adhesion between the defatted MBM and UHMWPE phases. This may be explained by the phase separation occurrence that was evident under the microscope (images are not provided here). Also, stiffness of the blended plastics depends on the ratio between the defatted MBM and UHMWPE in the blend: with increase in the stiffer (MBM) component, the storage

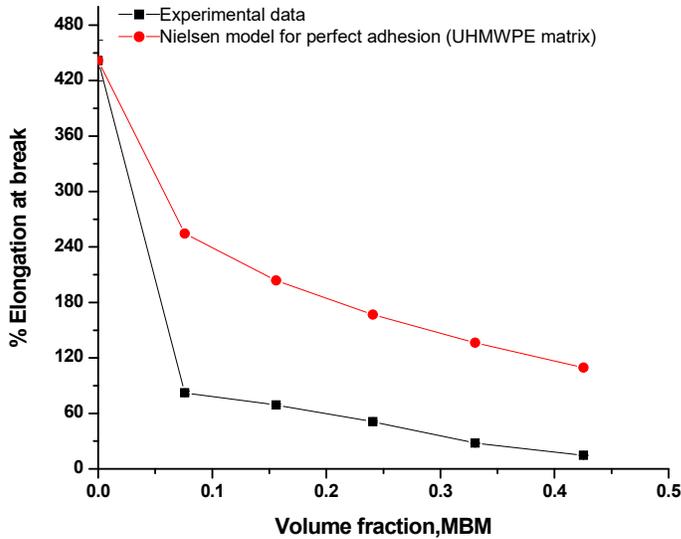
modulus of the plastic increases. The dependence deviates from the “mixing”, additive rule in a negative way. Storage modulus (**Figure 6a, b**) was found to decrease with increase in temperature. In general, the data indicate that removal of fat from MBM somewhat improves the adhesion between the phases in the blend.

**Figure 6:** Tensile modulus (a) and storage modulus at 75°C (b) and (c) 25°C of UHMWPE/MBM blends and comparison with Kerner theoretical model at each volume fraction.

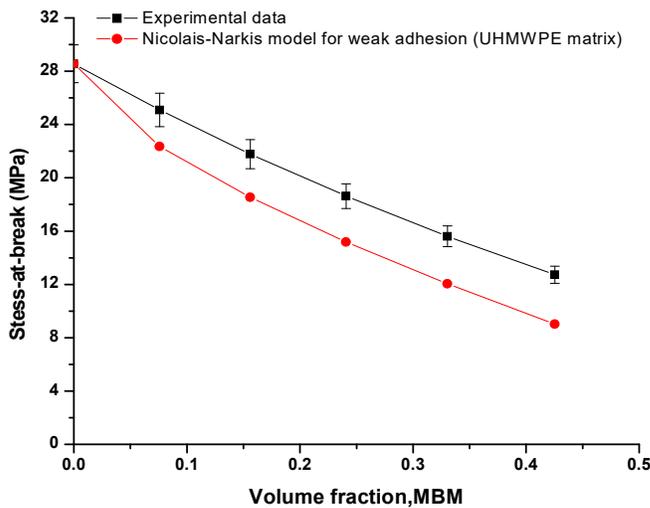


**Figure 7** shows the change in % elongation for UHMWPE/MBM blend .There is clear negative deviation from the mixing rule. The data was compared to Nielsen’s equation for perfect adhesion, **Equation 3**. The experimental data from **Figure 7**clearly indicate poor adhesion between MBM and UHMWPE blends. **Figure 8** shows that tensile strength for the blends of defatted MBM/UHMWPE. The experimental values lie above those predicted by **Equation 4**.the results indicating some level of adhesion between the components of the blend.

**Figure 7:** % Elongation at break for defatted MBM/UHMWPE blends and comparison with Nielsen theoretical model at each volume fraction.



**Figure 8:** Tensile strength for defatted MBM/UHMWPE blends and comparison with Nicolas-Narkis theoretical model at each volume fraction.



### **Impact and Significance:**

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. This has forced rendering industries to explore various alternative uses, such as biofuels and bioplastics. Manufacturing plastics from MBM or using MBM as filler for plastics are two potential ways to market MBM protein. We successfully produced plastic from MBM, and MBM/UHMWPE blend. Properties can be increased depending on an application. Using MBM as filler increase possible application area related with the polymer matrix. We envision that the area of application of the materials being developed will be in plastics for agricultural use. For example, flower pots, mulch film, nails to fix mulch film, plastic bags for trash can be made from the plastics. The major benefits are partial biodegradability from materials point of view and full biodegradability from the shape point of view. Additionally, since the MBM has a nutritious value, we expect that the products can fertilize soil.

### **Publications originated from the research supported**

Nzioki B. 2010 Biodegradable polymer blends and composites from proteins produced by animal co-product industry, MS Thesis, Clemson University.

Sharma, S. 2008. Fabrication and characterization of polymer blends and composites derived from biopolymers. PhD Dissertation, Clemson University.

Sharma, S., Hodges, J. N., Luzinov, I., 2008. Biodegradable plastics from animal protein co-products: Feathermeal, J. Appl. Polym. Sci. 110: 459-467.

Sharma, S., Hodges, J. N., Luzinov, I., 2008. Biodegradable plastics from animal co-product proteins and blends. Polymer Preprints 49(1): 903-904.

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