Biodegradable Plastics from Animal Protein Coproducts: Feathermeal

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ABSTRACT: This work describes the properties of plastics made from partially denatured proteins produced by the animal coproduct (rendering) industry and these plastics' fabrication. Specifically, plastic samples from partially denatured feathermeal protein were successfully produced by a compression-molding process. The modulus (stiffness) of the material obtained was found to be comparable with that of commercial synthetic materials, such as polystyrene, but was found to have lower toughness characteristics, which is a common phenomenon among plastics produced from animal and plant proteins. A reversible stress–strain property was observed over the yield region. Plastic-forming conditions for undenatured animal proteins, such as albumen and whey proteins, were also formulated for fabricating plastics out of these proteins' blends with feathermeal proteins. The resultant plastic samples that were developed of biomacromolecular blends, such as feathermeal/whey and feathermeal/albumen, demonstrated improved mechanical properties, specifically tensile strength, when compared with neat plastics from feathermeal proteins. The values for the stiffness of the feathermeal/whey blends deviated from simple mixing rule and showed a synergistic effect. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 459–467, 2008

Key words: biodegradable plastics; protein plastic; animal coproducts; denaturation; rendering

INTRODUCTION

Synthetic polymers, almost without exception, are not biodegradable. Polymers such as polyethylene, polystyrene, and polypropylene can persist in the environment for many years after their disposal. Therefore, the significance of the depletion of petrochemical resources, and the need for eco-friendly/biodegradable materials based on easily renewable natural resources, has necessitated the development of polymers from agricultural processing products.[1] Indeed, the only truly biodegradable plastics are those that can be consumed by microorganisms and reduced to simple, eco-friendly compounds. Biodegradable plastics are especially important in the production of articles that are unlikely to be recycled.[2]

The straightforward method of producing biodegradable plastics is by using natural renewable and biodegradable polymers based on starch, proteins, or cellulose.[3] In this respect, proteins are exceptionally versatile materials, both in the sources from which they can be obtained and in the wide variety of possible modifications, which can be helpful in tailoring their properties to the particular requirements of a specific application. They present significant advantages in that proteins are derived from a sustainable resource and can be processed in much the same way as conventional synthetic polymers. For instance, soy protein has been considered recently as an alternative to petroleum polymer in the manufacture of adhesives, plastics, and various binders.[4–8] It had been shown that plastics and polymer blends that were made from soy protein had high tensile strength and good biodegradable performance. In another study, compression molding of blends that contained either protein isolates or defatted whole flour of chickpea produced plastic of acceptable properties.[3] Protein isolates from sunflower, along with glycerol and water, were also used in various research studies to make thermal injection-molded biodegradable thermoplastics with better mechanical properties.[9] Injection-molded biodegradable plastic made from blends of corn gluten meal (a byproduct of the corn-based ethanol industries) was also developed.[10] In this communication, we report on yet another novel plastic materials produced from proteins. Specifically, we will describe the properties of plastics made from proteins produced by the animal coproduct (rendering) industry and the process of fabricating those plastics.

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Rendering, a process, which involves both physical and chemical transformation, is the recycling of raw animal tissue from food animals and waste cooking fats and oils. As a result, a variety of value-added products, such as bone meal, meat meal, poultry meal, hydrolyzed feathermeal, blood meal, and fishmeal, are produced. Without the continuing efforts of the rendering industry, the accumulation of unprocessed animal by-products would impede the meat industry and pose a serious potential hazard to animal and human health.[11] Recently, the outbreak of ''Bovine Spongiform Encephalopathy (BSE)'' or ''Mad Cow Disease'' in Europe has led to prohibition of the use of various proteins (e.g., meat and bone meal) from coproduct industries in ruminant feed in the United States and in any farm animal feed in the European Union. The excessive availability of these protein materials has encouraged the search for alternative uses of them, such as fabrication of biodegradable plastics.[12]

EXPERIMENTAL

Materials

Feathermeal protein was obtained from Fats and Proteins Research Foundation, VA. The reported protein content for feathermeal was 87.1%. The whey protein isolate (BiPro, Davisco Foods International) and albumin from chicken egg whites (A5253, Sigma-Aldrich), which were used for blending, had reported protein contents of 91% and at least 90%, respectively.

Preparation of defatted feathermeal protein and blends

The feathermeal protein, as received, was mixed with hexane, stirred for 15 min, and filtered to remove soluble fatty and objectionable contents; this process was repeated three times. The defatted protein was then left overnight in a fume hood to dry and was later vacuumed at a temperature of 50°C for 1 h, so as to ensure the complete evaporation of any residual solvent. The dried defatted feathermeal was manually ground and sieved using a stack of sieves (0.4 in, 600 micron, and 300 micron pore opening). The material's moisture content (MC) was analyzed and adjusted before molding. For whey/feathermeal and albumen/feathermeal blends, protein powders were mixed using a mechanical stirrer while adding water drop-by-drop to adjust the MC.

Specimen preparation

Type I specimens (ASTM standard D638-03) were molded from 3.6 g of feathermeal protein powder at 150°C and pressure of 20 MPa for 5 min on a hot press (Carver 60 Ton Economy Motorized Press). The mold was at room temperature during material filling. After the molding, the mold and specimens were cooled to $\leq$70°C under pressure before they were taken off and allowed to cool further at ambient conditions. Flash was removed by sanding the edges of the specimen with a grade-320 abrasive sandpaper. For whey/feathermeal and albumen/feathermeal blends, the samples were also molded at 150°C for optimal processing time and then cooled to $\leq$70°C under pressure before being taken off and allowed to cool further at ambient conditions.

Mechanical properties and morphology

Tensile stress, percent strain at break, and Young's modulus were measured using the Instron testing system (Model 1125) interfaced with computer operating Blue Hill software. 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} crosshead speed with a static load cell of 100 kN.

For analyzing the fracture surfaces, the specimens were sputtered with a thin layer of platinum and observed under a scanning electron microscope (SEM; Model S3500*N*, Hitachi, Japan) at an accelerated voltage of 20 kV.

Thermal analysis

Differential scanning calorimetry (DSC; Model 2920 TA Instruments) was carried out to determine the denaturing temperature (T_d) and the safe processing temperature window of the protein materials at a heating rate of 20°C min^{-1}. Thermogravimetric analysis (TGA) was carried out under N_2 purge (40 mL min^{-1}) at a heating rate of 20°C min^{-1} with a TA Instruments' Hi-Res TGA 2950 to study the thermal stability.

Moisture testing

A Sartorius MA50 moisture analyzer was used to analyze the moisture. For moisture testing, the samples were ground using liquid N_2. Moisture content was determined by eq. (1),

$$\mathrm{MC} = [(W_0 - W_{0d})/W_0] \times 100 \quad (1)$$

where W_0 is the initial weight of specimen and W_{0d} is the weight of specimen after drying.

RESULTS AND DISCUSSION

Plastics from feathermeal protein

Feathermeal protein can be described as an insoluble keratin protein-containing high amounts of cysteine

and sulfur-containing amino acids. The biomacromolecule is stabilized by disulfide bonds through cross-links with other intra or intermolecular cysteine fragments.[13] Feathermeal is required to be processed by pressure and temperature to destroy the disulfide bonds to denature the protein. During the rendering process, clean, undecomposed feathers from slaughtered poultry are pressure-cooked with live steam, partially hydrolyzing the protein and breaking the β-keratinaceous bonds that account for the structure of the feather fibers.

The as-received feathermeal had a MC of 5–6%, whereas the sieved defatted protein powder, after drying, had a MC of 9–10%. We supposed that the increase in the MC might be due to the removal of hydrophobic fatty contents (mostly saturated fats). The defatted feathermeal protein powder was analyzed by DSC and TGA. Even the feathermeal protein was thermally treated via the rendering process; DSC data [Fig. 1(A)] indicated the presence of a denaturation (unfolding) temperature ($T_d \sim 134^\circ C$) for the defatted feathermeal protein powder. Thus, the protein was not fully denatured during the rendering procedures, and further unfolding of the biopolymer took place upon heating.

The cooperative unfolding originates from disruption of the multiple small forces that maintain the secondary/tertiary protein structure.[14] Disruption of these forces alters the enthalpy of the system and causes the temperature to drop, because the unfolding process is generally endothermic. When a second DSC run was conducted for the feathermeal sample, no additional denaturation peak was observed. The results indicated that full denaturation was reached during the first DSC run. Table I shows the denaturing temperatures of various plant and animal proteins, as obtained by DSC measurements. The data suggest that additional denaturation of the feathermeal occurs in the temperature range that is typical for denaturation of other protein biomacromolecules. DSC measurements also provided important information on the nature of water incorporated into the feathermeal protein sample. In fact, an endothermic peak around 0°C, which would correspond to the melting of crystallizable (unbound) water, was not observed. Thus, it was concluded that the water molecules situated in the feathermeal were bound to the protein macromolecules.[15]

Figure 1(B) shows the weight loss of the feathermeal sample. The first weight loss occurred from room temperature to about 100°C. The loss was mainly caused by the water evaporation during denaturation.[16] In addition, TGA results (second weight loss) suggested that significant degradation of the protein was initiated at 220°C. Based on the results of the thermoanalysis, a certain molding cycle was accepted for the preparation of the plastic samples. Specifically, the defatted feathermeal protein powder was compression molded using a Carver press at a temperature of 150°C (between denaturation temperature and degradation temperature) and pressure of 20 MPa for 5 min and then cooled to 70°C under pressure. The water content for the plastic obtained was on the level of 4%.

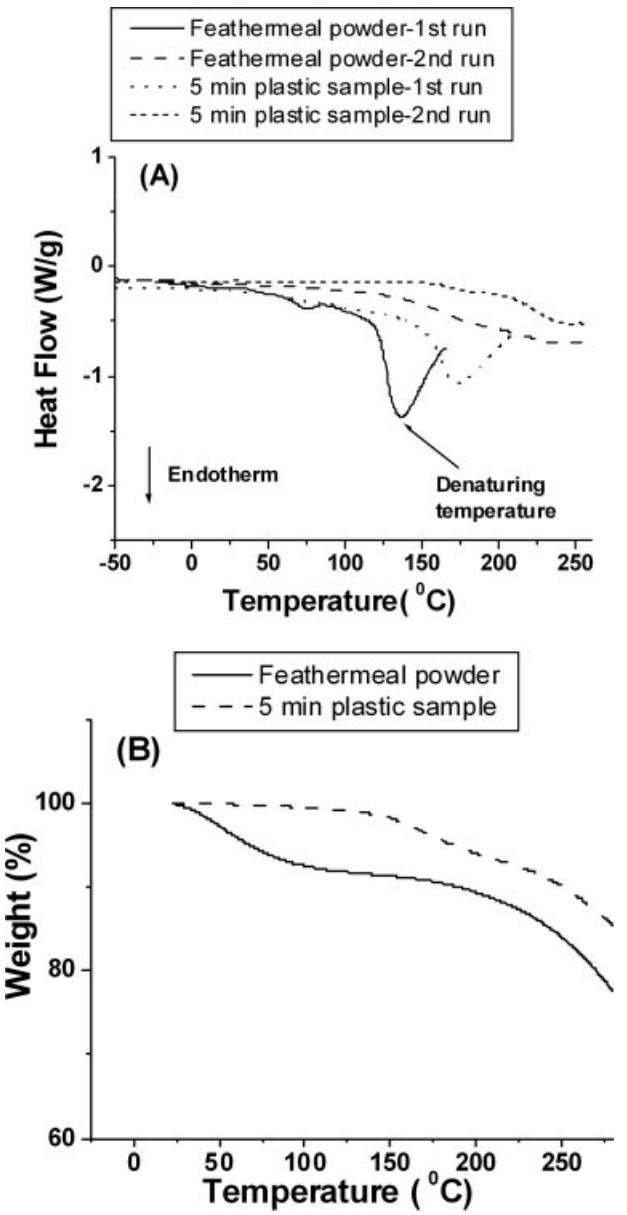

Figure 1 Thermal analysis of feathermeal protein powder and plastic samples produced at a temperature of 150°C and pressure of 20 MPa, followed by cooling to 70°C under pressure at 5 min of pressing: (A) DSC thermograms; (B) TGA thermograms. Note: In DSC graphs, first run is below the degradation temperature and little above the denaturation dip; therefore, first and second runs are not at same temperature range.

It was observed that, during the preparation of the plastic samples, there were irreversible rearrangements of protein macromolecules upon heat, pres-

TABLE I
Denaturing Temperature of Various Plant and Animal Proteins from DSC Studies

Protein	Denaturation temperature T_d (°C)	Reference
Corn zein isolate	~ 150°C	29
Wheat glutenin	65°C and 85°C	30
Soy protein isolate	80°C and 95°C	31
Fowl feather keratin (Dry)	170–200°C	32
Fowl feather keratin (Wet)	110–160°C	32
Cottonseed isolate	~ 140°C	33
Whey protein concentrate	~ 75°C	34
Ovalbumin from chicken egg white	84°C	35
Feathermeal protein	134°C ± 21°C	This study
Albumin from chicken egg white	136.5°C ± 3.0°C	This study
Whey protein isolate	135.6°C ± 1°C	This study

sure, and time. In fact, the original endothermic peak due to the denaturation (~ 132°C) was not detected for the plastic samples obtained [Fig. 1(A)]. Conversely, an endothermic peak at roughly 171°C was found for the plastic specimens. The result indicates that another type of folded structure is formed during the plastic preparation. We suppose that the formation of multiple hydrogen bonds between amino, carboxy, and hydroxy amino acid residuals are responsible for the structurization. Interestingly, the second DSC run [(Fig. 1(A)] shows no peak around 171°C for the feathermeal plastic, pointing to the conclusion that pressure might be responsible for the structurization of the protein material during the plastic fabrication.

TGA results showed that a different weight loss pattern was observed for the plastic samples [Fig. 1(B)] in comparison with the original feathermeal material. Specifically, the first (water) weight loss occurred over a more extended temperature range: from room temperature to about 210°C. The slowdown of the water loss can be explained by the denser structure of the plastic sample when compared with the protein powder. The temperature of degradation, however, was virtually unaffected by the compression molding.

Figure 2(A) shows the typical stress–strain diagram for the tested dog bone samples made from the feathermeal plastic. The first region, where the stress (σ) increases linearly with strain (ε), is a region of elastic deformation; it is followed by plastic yield and strain hardening regions. We attributed the yield point to the break in hydrophobic interaction and hydrogen bonds of folded protein macromolecules. Remarkably, this phenomenon in the yield region is reversible in nature, as can be observed from the cyclic loading testing of plastic samples [Fig. 2(B)]. It appears that biomacromolecules, which constituted the sample, fold back when the sample is unloaded before the break. This original mechanism of dissipating energy can be extremely useful if the plastic is subjected to a cycling loading during use.

Figure 3 shows the corresponding SEM micrograph of the fracture surfaces (from the tensile test), which indicate the brittle nature of the fracture. The stress at break, strain at break, and modulus were measured to be 9.2 MPa, 1.40%, and 2.20 GPa, respectively. The observed mechanical properties

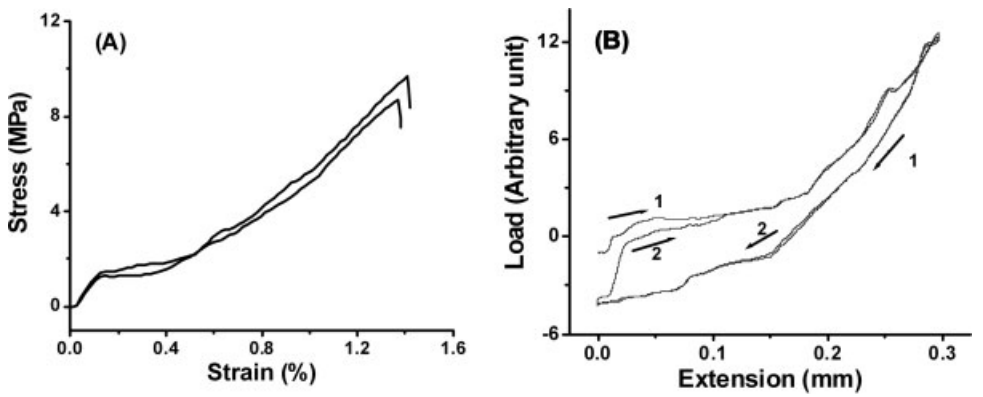

Figure 2 A: Stress–strain curve for the compression-molded feathermeal plastic; (B) Cyclic loading testing of the feathermeal samples, produced at a temperature of 150°C and pressure of 20 MPa for 5 min, followed by cooling to 70°C under pressure.

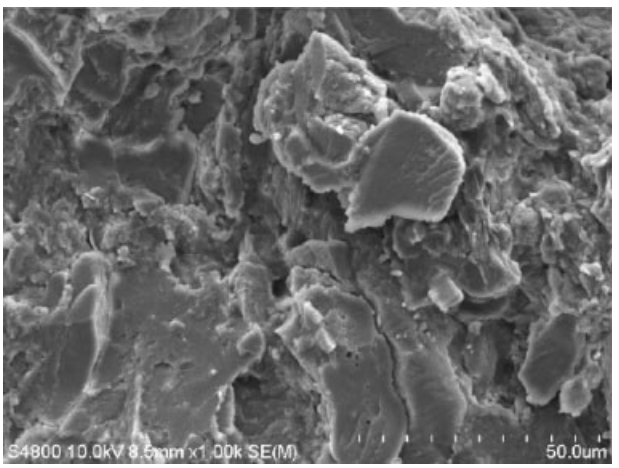

Figure 3 Scanning electron microscopy (SEM) micrograph of feathermeal plastic produced at a temperature of 150°C and pressure of 20 MPa, followed by cooling to 70°C under pressure.

(high stiffness accompanied by low extensibility) are in the range of the values that are typically observed for bioplastics fabricated from unplasticized proteins. For instance, for plastic from soy protein, the stress at break, strain at break, and modulus were reported to be 35 MPa, 2.6%, and 1.63 GPa, respectively.[17] The properties of plastic made from soy protein are somewhat better in terms of strength and elongation. We associate this difference with the fact that protein plastics are typically prepared from biomacromolecules, which are thermally untreated and possess their native conformation. In our case, we dealt with protein that had been subjected to denaturation procedures before the fabrication of the plastics. Accordingly, to improve their properties, animal coproduct proteins can be mixed with proteins that possess a lower level of denaturation and demonstrate better properties.

Plastics from blends containing feathermeal protein

One of the most efficient routes for obtaining plastics with improved properties is polymer blending, in which two or more polymers are combined in one polymeric material. For instance, blends of synthetic polymers and natural polymers (polysaccharide and protein based) were used to produce totally and partially degradable blends.[18] For a polyblend, a weakness in one component can, to a certain extent, be camouflaged by strength in the other constituting part.[19] In general, the blends can be divided into homogeneous (miscible, one phase) and heterogeneous (more then one phase). In a homogeneous blend, the components of the blend virtually lose part of their identity. The final properties of a miscible blend usually follow the so-called mixing rule (the arithmetical average of blend components). In a phase-separated blend, the properties of all blend components are present, and the final performance of the blend is very dependent on the size of structural elements and the adhesion at the interface. In general, a majority of immiscible blends are incompatible and demonstrate negative deviation from the mixing rule because of gross phase morphology and low interfacial adhesion. These blends are in many ways useless if they are not compatibilized.[19] In a few exceptional cases (some) properties of a compatible blend may be better than those of the individual components. Namely, a synergistic effect, which is sometimes difficult to predict, is observed.

For the case of blending, as we consider in this work, where (partially denatured and nonsoluble) feathermeal is blended with (nondenatured and water soluble) proteins, a heterogeneous polymer blend ought to be obtained. The protein–protein blend is supposed to be compatible, because the proteins possess complementary reactive functional groups such as amino, carboxy, and hydroxy. Owing to the reactions between the functionalities at the phase boundary, strong interfacial adhesion should be readily achieved after annealing of the samples at elevated temperatures.

We selected two commercially available, nondenatured and pure natural proteins, such as albumen (chicken egg white) and whey, for the blending experiments. Whey and albumen proteins are already used in various technical applications, such as adhesives and coatings.[20,21] The albumen and whey powders, as received, had a MC of 5.20 and 7.90%, respectively. This was mainly due to the bonded water as is also apparent from DSC and TGA graphs in Figure 4. Figure 4(A) shows DSC thermograms for the undenatured albumen and whey protein powders, and it can be discerned that the albumen and whey proteins denature at a temperature of roughly 130–150°C. This is clearly not the degradation temperature, which onsets around 250°C, as can be observed in Figure 4(B).

It was previously reported that to produce a plastic with acceptable performance from nondenatured proteins, water or other molecules of low molecular weight should be added to act as a plasticizer, improving the processability and thermoplasticity of the protein during molding.[4,5,22-24] Indeed, as received, the whey and albumen proteins did not produce plastic samples when compression molded at elevated temperatures. We varied the amount of water that was added to the proteins before molding and determined that the optimal MC for making plastics from whey and albumen was 25% of the total weight (protein powder plus water). Therefore, in our experiment, the albumen and whey powder with 25% w/w of water were compression molded

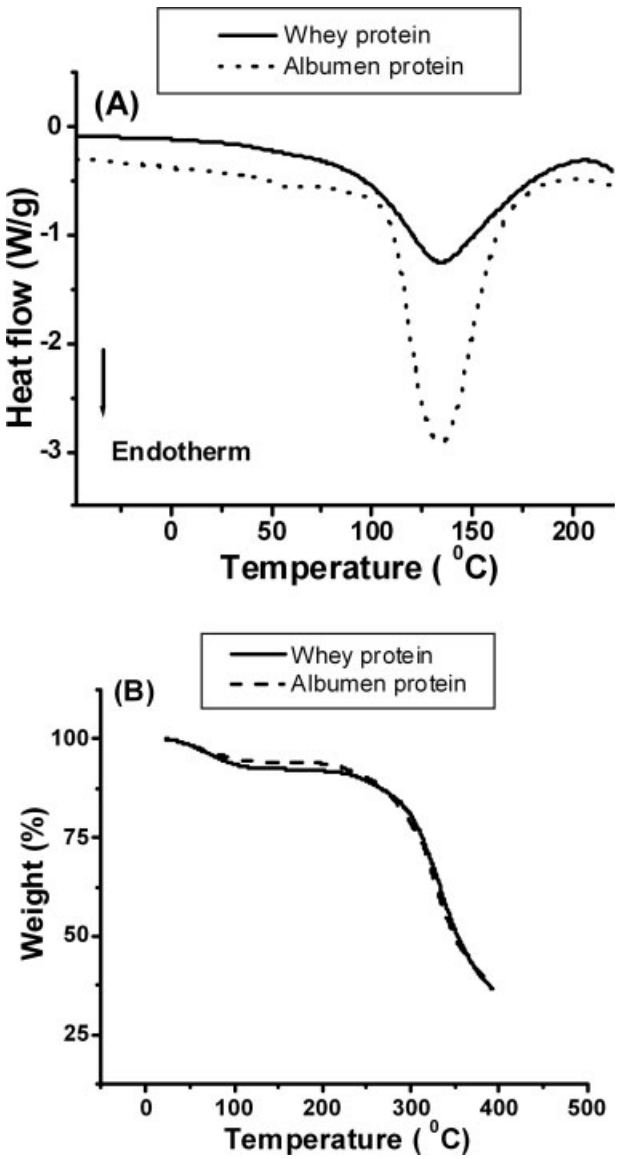

Figure 4 Thermal analysis of albumen and whey proteins powder: (A) DSC thermographs; (B) TGA thermographs.

at a temperature of 150°C and pressure of 20 MPa for 5 min, followed by ambient cooling. It was found that samples that were left for drying under ambient conditions showed an increase in modulus and stress at break and a decrease in strain at break over time, due to the evaporation of residual water content from the molded samples. To standardize the drying conditions, each sample containing whey or albumen proteins was dried in an oven at 50°C overnight. This drying procedure resulted in the samples having water contents of 7.9% and 7.2% for whey and albumen samples, respectively.

The stress at break, strain at break, and modulus were measured to be 19 MPa, 5.8%, and 1.4 GPa and 16.7 MPa, 2.8%, and 2.4 GPa for the whey and albumen plastics, respectively. In general, the plastics obtained showed higher strength and elongation than did the feathermeal materials. On another hand, the stiffness of the feathermeal plastic was somewhat higher. To compare the properties of the whey/albumen and feathermeal plastics directly, the procedure for preparation of the feathermeal samples was modified to include annealing overnight at 50°C. The change in fabrication resulted in the alteration of mechanical properties of the feathermeal plastic. The stress at break, strain at break, and modulus were determined to be 5.7 MPa, 1.1%, and 2.87 GPa. The MC for the plastic was on the level of 4%. The annealing increased the modulus of the feathermeal plastic, but it caused a significant decrease in strength and elongation. Evidently, plastics obtained from the different biomacromolecules have complementary properties, and blending of the proteins should result in an improvement of the mechanical performance of the feathermeal polymeric materials.

Mixtures of feathermeal/albumen and feathermeal/whey proteins in 50 : 50% w/w ratio were prepared to obtain polymer blends from the biomacromolecules. Specifically, the defatted feathermeal protein powder (MC of 10%) was dry blended with the natural proteins using mechanical stirrer; water was then added to the mixture (up to 25% on dry weight of albumen and whey proteins) drop by drop. The mixture was kept overnight for equilibration of water. A DSC study of the protein mixtures showed that there was practically no crystallizable (unbound) water in the samples. Therefore, the water molecules situated in the mixtures were bound to the protein macromolecules. The blend samples were molded to form plastic samples at a temperature of 150°C and pressure of 20 MPa for 5 min, then cooled to 70°C under pressure, and dried in an oven at 50°C overnight.

The mechanical properties from the static testing showed significant improvement when compared with unmodified feathermeal protein samples (Fig. 5). In general, addition of the nondenatured proteins to the feathermeal material improved the elongation at break and the stress-at-break of the plastics. In fact, strain-at-break for the blend increased more than 1.5 times when compared with plastic made from feathermeal alone at the same conditions. Significant improvement was found in the strength of the blended material. The stiffness of the polymer blend made with albumen was slightly lower than expected, because pure albumen plastic possessed lower stiffness than the pure feathermeal plastic. The blend of feathermeal and whey proteins demonstrated the highest breaking stress and a Young's modulus of 12.6 MPa and 3.34 GPa, respectively. This blend demonstrated a synergistic effect in terms of stiffness, because the elastic modulus of the blend was higher than the moduli of pure components (2.87 GPa for the feathermeal plastic and 1.4 GPa for

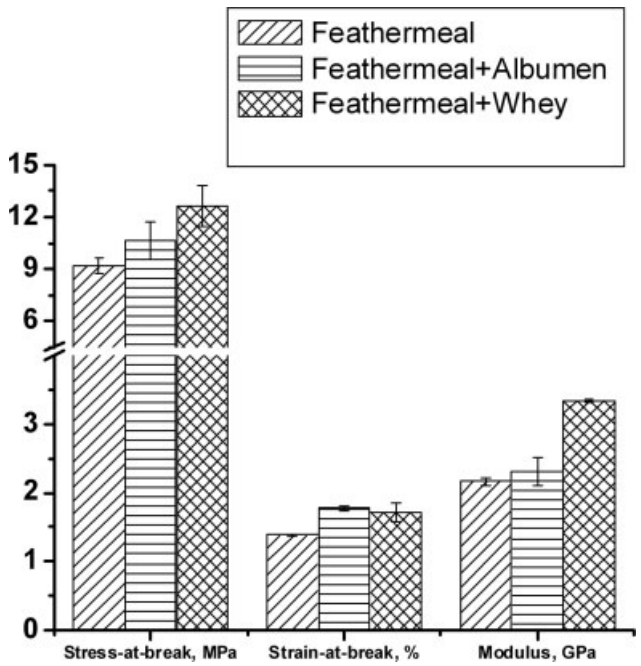

Figure 5 Mechanical properties of plastics produced from feathermeal and the blends of feathermeal/albumen and feathermeal/whey (50% : 50% w/w ratios) proteins, molded at a temperature of 150°C and pressure of 20 MPa for 5 min, followed by cooling to 70°C under pressure, and overnight drying in an oven at 50°C. Error bars are ± one SD; there were four replicates at each activity.

the whey plastic). The obtained results indicated that the blending of feathermeal with whey protein has definite potential. To evaluate the properties of the blend further, we prepared plastics containing different ratios of biomacromolecular materials. We attempted to model the behavior of the blends using known relationships that have been used to predict properties of polymer blends. The relationships were developed for spherical inclusions distributed in a matrix, but as a first approximation are often used for systems, where inclusions are not spherical in shape.

Figure 6 shows that the stiffness of the blended plastics depends on the ratio between feathermeal and whey in the blend. With the increase in the (stiffer) feathermeal component, the elastic modulus of the plastic increases. The dependence deviates from the simple ''mixing,'' additive rule in a positive way, indicating a clear synergistic effect, in which the properties of the blend are better than those of the individual components. Interestingly, the effect is observed in the region of possible phase inversion, where the ratio between the components is close to 1 : 1.

For polymer blends containing nearly spherical particles of any modulus, a Kerner and Hashin equation has been used to model the level of stiffness. The well-established form of the Kerner equation, which considers the dispersed phase as spheroidal in shape, has the following form:[25]

$$E = E_1 \frac{\frac{\phi_2 E_2}{(7-5\nu_1)E_1+(8-10\nu_1)E_2} + \frac{\phi_1}{15(1-\nu_1)}}{\frac{\phi_2 E_1}{(7-5\nu_1)E_1+(8-10\nu_1)E_2} + \frac{\phi_1}{15(1-\nu_1)}} \quad (2)$$

where E, E_1, and E_2 are the moduli for the binary blend, the matrix, and the dispersed phase, respectively; ϕ_1 and ϕ_2 are the volume fractions of the matrix and the dispersed phase, respectively; ν_1 is the Poisson ratio for the matrix (To estimate the volume fractions we considered density of protein material to be 1 g cm^{-3}.) This equation is valid in case of an ideal stress transfer through the interface (strong adhesion between the phases). If no stress is transferred (i.e., there is no adhesion between the phases), the Kerner equation is simplified, because E_2 is then assumed to be zero:

$$E = E_1 \frac{1}{1 + (\phi_2/\phi_1)[15(1-\nu_1)/(7-5\nu_1)]} \quad (3)$$

Figure 6 shows that the theoretical prediction by eqs. (2) and (3) indicate that there is good adhesion between feathermeal and whey protein phases. This may be explained due to the functional compatibility between proteins (acid-basic interaction) and increased amide links from free COOH and NH_2 groups. The stiffness of the polymer blend in the

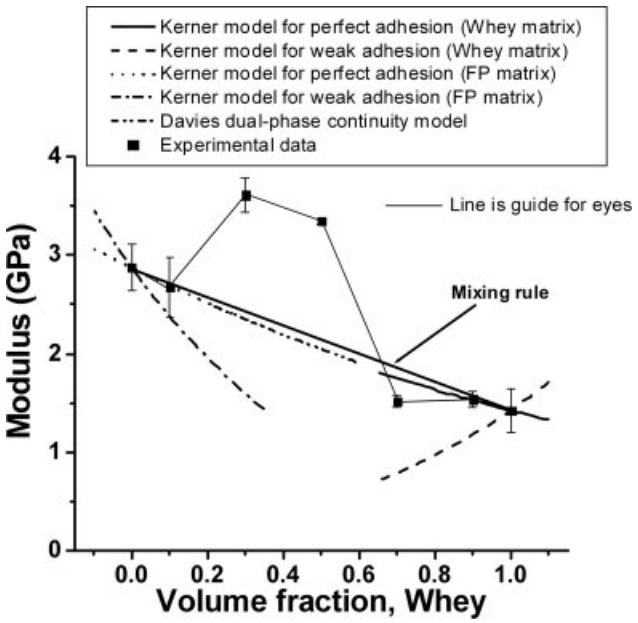

Figure 6 Tensile modulus of the feathermeal/whey blends and comparison with theoretical models with four replications at each volume fraction, error bars are ± one SD. Note: All samples were molded at a temperature of 150°C and pressure of 20 MPa for 5 min, followed by cooling to 70°C under pressure, and overnight drying in an oven at 50°C. Note: FP, feathermeal protein.

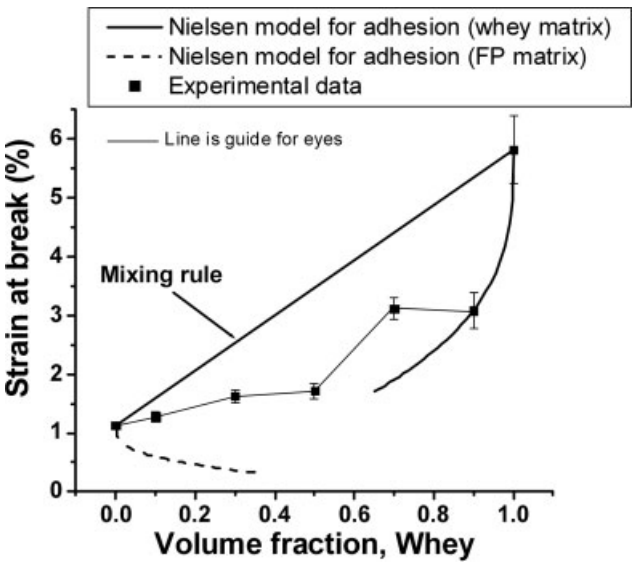

Figure 7 Tensile strain at break of the feathermeal/whey blends and comparison with theoretical models with four replications at each volume fraction; error bars are ± one SD. Note: All samples were molded at a temperature of 150°C and pressure of 20 MPa for 5 min, followed by cooling to 70°C under pressure, and overnight drying in an oven at 50°C. Note: FP, feathermeal protein.

phase inversion region, where dual-phase continuity is observed, can be approximated by the Davies equation,[26] showing that the moduli raised to the one-fifth power as shown in eq. (4).

$$E^{1/5} = \phi_1 E_1^{1/5} + \phi_2 E_2^{1/5} \tag{4}$$

For the projected phase inversion region, experimental results lie above the theoretically predicted ones from Davies dual-phase continuity model, suggesting the presence of synergistic effect.

Figure 7 shows the change in elongation (or % tensile strain at break) for the feathermeal/whey blend. There is a clear negative deviation from the mixing additive rule. The elongation at break can be evaluated (for polymer composites and blends) using a Nielsen equation.[27] According to Nielsen, in general, the introduction of a dispersed phase into a matrix causes a dramatic decrease in elongation to break. If there is good adhesion between the phases, the following equation is approximately correct:

$$\varepsilon_C = \varepsilon_0 \left(1 - \phi^{1/3}\right) \tag{5}$$

where ε_c is the elongation to break of the blend and ε_0 is the elongation at break of polymer constituting the matrix. There is a clear indication of good adhesion between feathermeal protein and whey polymer, as the experimental data are in close agreement or are higher than the values predicted by eq. (5) (Fig. 7). The obtained results are in accord with the elastic modulus calculations.

The presence of dispersed phase is also often expected to decrease the tensile strength of a matrix material. According to Nicolais and Narkis,[28] the tensile (yield) strength (σ) of a composite with ''uniformly'' distributed spherical filler particles of equal radius can be estimated by eq. (6).

$$\sigma_C = \sigma_m (1 - a\,\phi^b) \tag{6}$$

where σ_c is the composite tensile strength, σ_m is the polymer matrix tensile strength, a and b are constants, and ϕ is the volume fraction of filler. Constants a and b depend on stress concentration and dispersed phase geometry, respectively. For the spherical fillers, if there is no adhesion with matrix and if the fracture goes through the filler-matrix interface, the above equation becomes

$$\sigma_C = \sigma_m \left(1 - 1.21\,\phi^{2/3}\right) \tag{7}$$

According to Piggot and Leidner, the strength at break can be described by first power law equation:

$$\sigma_C = \sigma_m (1 - \phi) S \tag{8}$$

where parameter S accounts for the weakness in structure due to stress concentration points at polymer-filler interphase. When S is unity, there is no stress concentration effect, implying better adhesion.

Figure 8 shows the tensile strength results for feathermeal/whey blends. The values of the stress-at-break are generally (beside one composition) sig-

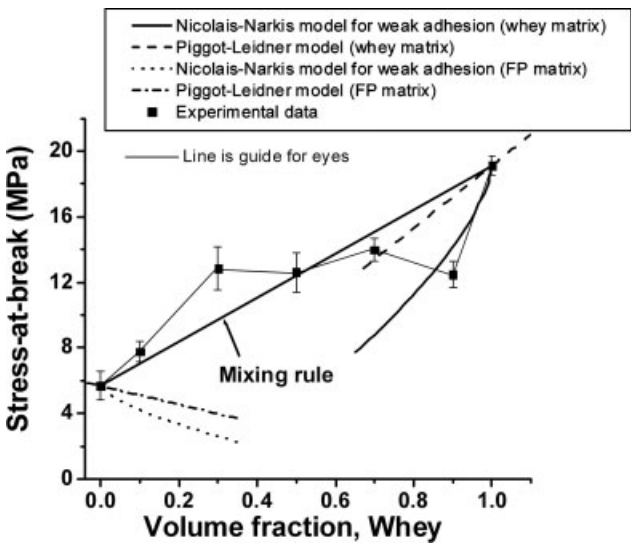

Figure 8 Tensile strength of the feathermeal/whey blends and comparison with theoretical models with four replications at each volume fraction; error bars are ± one SD. Note: All samples were molded at a temperature of 150°C and pressure of 20 MPa for 5 min, followed by cooling to 70°C under pressure, and overnight drying in an oven at 50°C. Note: FP, feathermeal protein.

nificantly above those predicted by eqs. (7) and (8). In fact, the strength of the blend is close to the ''mixing'' rule. The results once again indicate that there is a strong interaction between the components of the blend.

CONCLUSIONS

Plastic samples from partially denatured feathermeal protein were successfully produced by the compression-molding process. The modulus (stiffness) for the material obtained was found to be comparable with that of commercial synthetic material but with lower toughness characteristics, which is a common phenomenon among plastics, produced from animal and plant proteins. A reversible stress–strain property over the yield region was observed. Plastic forming conditions for undenatured animal proteins, such as albumen and whey proteins, were also formulated for developing plastics out of these protein's blends with feathermeal proteins. The resultant plastic samples made from these biomacromolecular blends demonstrated improved mechanical properties when compared with neat plastics from feathermeal proteins. The results were interpreted in terms of theoretical models to describe mechanical properties such as extensibility, tensile strength, and stiffness of the plastics made out of feathermeal/whey blends at various volume ratio. The values for the stiffness of the feathermeal/whey blends deviated from the simple mixing rule and showed a synergistic effect.

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