

Thermal Processing and Properties of Bioplastic Sheets Derived from Meat and Bone Meal

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ABSTRACT: Chemical modification of plasticized meat and bone meal (MBM) and its thermal processing into bioplastic sheets is reported. Specifically, MBM plasticized with 30 wt% glycerol and modified with calcium hydroxide (CH) (0, 3, 7, and 10 wt%) was batch compounded at 100°C, 15–30 min, and 60 rpm followed by thermal compaction at 140°C to produce sheets. The effect of CH content on the chemical structure, processability, and tensile properties (static and dynamic) of modified MBM sheets were studied. Fine particle size of MBM and moderate environment humidity produced well-consolidated sheets. Increase in CH content to about 7 wt% was found to increase tensile strength and modulus, whereas the strain to failure decreased. Fourier transform infrared spectroscopy analysis of modified MBM sheets showed that the changes in mechanical properties could be attributed to increased interactions between protein chains, which were further aided by the precipitation of the fat portion of MBM. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 256–263, 2013

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INTRODUCTION

The increasing restriction on the use of meat and bone meal (MBM) for animal feed applications, because of its association with the Bovine Spongiform Encephalopathy disease, has left a large source of low-value biomass available.^{1,2} Efforts are under way for alternative nonfeed applications of this material in value-added products.^{3–5} Prior studies have reported potential application of MBM as a fuel and adhesive.^{3,4} Because of its protein content, use of MBM as a protein concentrate source and bioplastic has also been reported.^{4,5} In addition, MBM is derived from a renewable source and is biodegradable, making its use in biodegradable plastic applications attractive as it can mitigate some of the environmental concerns associated with petroleum-based synthetic plastics.

Studies on biodegradable materials made from blood meal, feather keratin, gelatin, feather meal, soy, and zein proteins have been reported in various literature studies.^{6–15} Processing of protein-based films and sheets by thermal processing requires plasticizers, which intersperse among and within polymer chains, and disrupt hydrogen bonds thereby spreading the chains apart.¹⁶ Use of polyols (e.g., glycerol and sorbitol) increases molecular mobility, which decreases stiffness and increases ductility of the biomaterial by lowering the glass tran-

sition temperature.¹⁷ Furthermore, nonfeed applications like bioplastic sheets require denaturation of proteins to occur, and are aided by the presence of small amount of water (~5%).¹⁸

In addition to plasticizers and water, other reagents such as chemical denaturants, reducing agents and crosslinking agents have also been added to optimize protein configuration and improve properties of resulting bioplastics.^{16,19} Calcium ions are known for influencing mechanical properties of biological materials.²⁰ In solvent processing, addition of calcium chloride to protein solutions has been shown to have significant effects on the mechanical and water sorption properties of resulting films.^{21,22} The tensile strength of such films is reported to range from about 1 to 17 MPa at 25°C, and 50% RH. The water vapor permeability was reported to range from 13 to 262 g mm/m² day kpa.¹⁶

Literature studies indicate that the mechanical properties of polymers are determined by chemical bonding and molecular structure.²³ Secondary molecular structure of protein can be determined by Fourier transform infrared spectroscopy (FTIR). Amide I and amide II bands arise from bonds that link the amino acids of the protein.²⁴ Amide I is because of carbonyl stretching in the region of 1600–1700 cm⁻¹; whereas amide II is because of N–H bending vibrations in the region 1500–

1560 cm^{-1} .²⁵ Literature studies on the chemical modification of soy flour for adhesive preparation showed that FTIR can be used to follow chemical structure changes of the protein and reveal properties of the final adhesive.²⁶ FTIR analysis of amide I band of thermoplastic processed blood meal, showed a decrease in β -content hence decreased molecular order with addition of urea.⁷

The films reported in the above studies were produced primarily from protein isolates, concentrates or extracts with protein content greater than 70%. However, such purified forms are also expensive. In contrast, MBM is a low-cost biomaterial with a protein content of about 50%, and has a potential as a film precursor. Literature studies on the use of MBM as a bioplastic have explored blending the MBM with expensive sodium caseinate and extruding the mixture into a dog chew toy.⁵ Also investigations of effect of calcium ions on protein film formation have been limited to solution casting process.²¹ Therefore, this article was directed towards a cost-competitive, thermoplastic processing route of MBM-based sheets, but without the use of synthetic polymers or expensive additives. The specific objectives were to (i) evaluate the effect of chemical modification of MBM by glycerol and calcium hydroxide (CH) on sheet formability, and (ii) characterize the mechanical properties and microstructure of the resulting bioplastic sheets for potential geo-structural applications.

EXPERIMENTAL

Materials and Processing

MBM protein (Darling International) was used throughout this study. It is an animal co-product with an approximate composition of 50% protein, 8–12% fat, 4–7% moisture, and 35% ash. Because as-received MBM contains large bone particles, it was milled for further processing. The milled MBM sample was sieved through two sieve plates to obtain: (a) a coarse grade that was the bottom product of sieving through a 16 mesh sieve (1 mm opening) for a $97 \pm 2\%$ yield, and (b) a fine grade that was the bottom product of sieving grade (a) further through a 60 mesh (250 μm opening) that resulted in a yield of $65 \pm 2\%$. Initial studies were conducted on the coarse grade, but most of later studies focused on the fine grade.

Glycerol (SIGMA-Aldrich) was added to the MBM as plasticizer at 15, 30, and 45 wt% compositions. Following the determination of plasticizer content, the next step was the CH modification of MBM at 0, 3, 7, and 10 wt %. CH (VWR International) was initially dissolved in glycerol to form a viscous white paste that was then manually mixed with MBM to form a dough. The dough was intensively compounded in a Haake Rheomix 600 batch mixer at temperatures ranging between 80°C and 120°C for a mixing time of 15–30 min forming consolidated rubbery chunks. Blending and compounding was also done with the fine MBM to study the influence of particle size on the sheet formation and mechanical properties.

The rubbery chunks (12.5 g) were thermally compacted in an open mold 100 mm \times 100 mm \times 0.6 mm using a press (Carver Model 389.4PR1B00) at 6 MPa and 140°C. A holding time of 2 min was allowed for heat transfer to the mold and subse-

quent softening of the blend. The final load was applied for 2 min and the sample was subsequently cooled to nominal ambient conditions (40°C) under pressure before removing the sheet from the press. Optical microscopy (Olympus BX60) and scanning electron microscopy (SEM—Hitachi S4800) were used to analyze the texture and surface characteristics of the sheets.

Thermal Analysis

Thermogravimetric analysis was conducted using a PerkinElmer Pyris 1 instrument. The samples were heated in an aluminum pan under air atmosphere from 26°C to 400°C at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was performed with a TA instrument MDSC 2920 from -100°C to 240°C at a heating rate of 20°C/min under a nitrogen atmosphere. Sample weight was nominally 5 mg.

Fourier-Transform Infrared Analysis

Fourier-transform infrared (FT-IR) analysis was conducted using a Nexus 870 FT-IR ESP, Nicolet and OMNIC version 5.1 analysis software. The spectra of all the sheets, MBM powder, and glycerol were obtained using a Germanium ATR (attenuated total reflectance) accessory over a spectra range of 4000–600 cm^{-1} . For each composition, spectra were obtained at three different points of the sheet and 32 scans with 8 cm^{-1} resolution were averaged.

Tensile Properties

Static Tensile Test. Tensile tests were conducted following the ASTM D638-10 procedure except that rectangular strips were used rather than dog-bone specimens. The samples were nominally 0.6 mm thick, 1.3 cm wide and 11.4 cm long, and the gauge length was set at 5.7 cm. Mean thickness of the samples was obtained from five points with a Nikon Digimicro, MF-5-01. Mechanical testing of the sheets was performed at a cross-head speed of 0.25 cm/min (Applied Test Systems, Series 900). A minimum of five replicates for each composition were tested to calculate average values. Samples were conditioned for 24 hours at RH levels of 20% and 50%. Conditioning was also done in a vacuum oven at 50°C (~ 75 cm Hg vacuum) for 24 h to obtain almost dry sheets.

Dynamic Tensile Test. TA Instruments RSA III rheometer was used for the dynamic mechanical testing using an initial length of 28 mm, a width of 12.7 mm, and a thickness of 0.6 mm. An auto-tension adjustment was applied to the samples during testing. They were preconditioned in an oven under 75 cm Hg of vacuum at 50°C for 24 h. The dynamic frequency measurements were obtained at 0.05% strain and 25°C with the frequency varied from 0.1 to 20 rad s^{-1} . The dynamic temperature ramp measurements were conducted at 0.05% strain and a frequency of 6.3 rad s^{-1} .

RESULTS AND DISCUSSION

Sheet formation from protein material requires the addition of plasticizers, which lower the glass transition temperature of the protein and enable them to be processed at temperatures below the decomposition temperature.²⁷ Figure 1(a) displays the thermograms for as-received MBM powder and plasticized MBM (30 wt % glycerol). For the MBM powder, the thermogram shows two mass loss steps: one below 100°C attributed to water

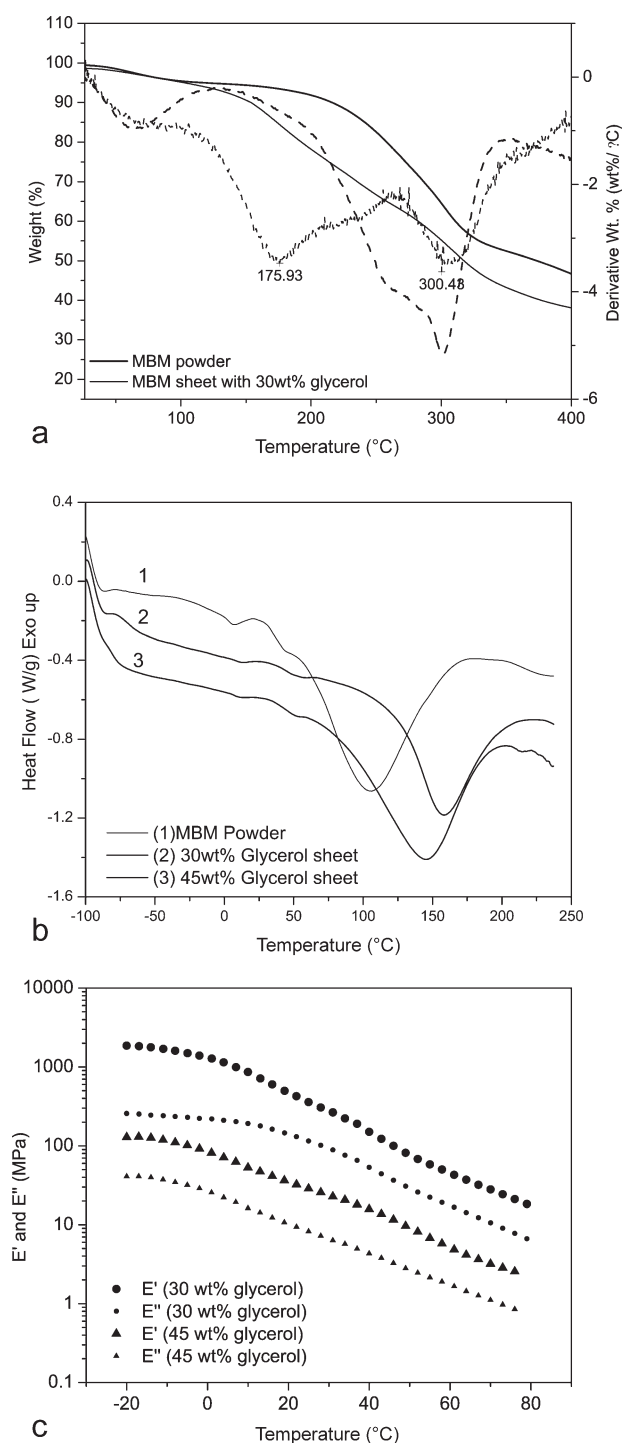


Figure 1. (a) Thermogravimetric analysis of MBM powder and MBM sheet containing 30 wt % glycerol conducted in air atmosphere at a heating rate of 10°C/min. (b) DSC thermograms at a heating rate of 20°C/min under a nitrogen atmosphere for (1) as-received MBM, (2) MBM sheet plasticized with 30 wt %, and (3) MBM sheet plasticized with 45 wt % glycerol. (c) Dynamic storage and loss moduli as a function of temperature for 30 and 45 wt % glycerol plasticized MBM sheets.

evaporation, and the second in 200–300°C range because of the degradation of proteins and evaporation of low molecular weight components. This behavior is consistent with that reported by

other researchers.^{28,29} Plasticized MBM showed initial mass loss just under 100°C followed by a continuous mass loss in 120–175°C range with a significant loss observed starting at about 175°C. Therefore, compounding and thermal compaction of plasticized MBM was conducted at a temperature below 150°C.

Figure 1(b) displays the DSC thermograms of as-received MBM and that of sheets plasticized with 30 and 45 wt % glycerol. All thermograms showed thermal transitions between -2°C and 50°C and a large endothermic peak between 50°C and 200°C . MBM powder showed an endothermic peak at about 0°C from the melting of frozen water in the sample. It also shows a weak glass transition (T_g) between 30°C and 40°C . Plasticized MBM samples also showed a small endotherm at 0°C followed by a T_g between 35°C and 50°C . The large endothermic peak observed between 50°C and 200°C for MBM powder and the plasticized MBM is a combined effect of water loss and protein denaturation. There is a shift of the water loss–protein denaturation peak to higher temperature from 106°C (observed for MBM powder) to 145°C and 158°C for 45 and 30 wt % glycerol content, respectively. Similar observations have been made by other researchers on these transitions that result from proteins that have denatured (unfolded) during the compounding and thermal compaction steps.^{11,30} The low T_g observed for MBM is largely attributed to the higher moisture content of the MBM powder.

Figure 1(c) displays the dynamic storage and loss moduli of MBM sheets plasticized with 30 and 45 wt % glycerol. As expected, both samples showed a decrease in the dynamic moduli with increasing temperature, but the storage modulus remained higher than the loss modulus. For the 30 wt % glycerol sheet, the storage modulus was 1855 MPa at -20°C , which is more than an order of magnitude higher than a value of 124 MPa displayed by 45 wt % glycerol sample. This significant difference is observed over the entire test temperature range. Therefore, a plasticizer content significantly greater than 30 wt % produced soft, weak sheets, whereas that much less than 30 wt % (i.e., 15 wt %) was found to result in insufficient consolidation. Recent work by Zeller et al. also found DMA as a useful technique to establish optimal plasticizer content.³¹ Thus, based on the consolidation level, microscopy, and DMA of consolidated sheets, a 30 wt % glycerol composition was established as being adequate. Further, the DSC thermograms had revealed that MBM sheets plasticized with 30 wt % glycerol had a denaturation temperature of about 160°C . Thus, a plasticization level of 30 wt % (glycerol) allowed sufficient motor torque and specific energy input for protein interaction while allowing processability below 150°C , and was used throughout the rest of the study.

Initial processing experiments conducted on as-received MBM produced sheets that contained numerous holes. Therefore, milling and sieving was conducted (as described in the experimental section) to obtain coarse and fine grades of the milled sample. Figure 2 shows the optical micrographs over a 4 mm^2 area of MBM-glycerol sheets produced from as-received, coarse, and fine MBM. The regions identified by circles illustrate intense transmitted light because of the presence of pin-holes in the sheet. For the given area, as-received MBM sheets had numerous holes (~ 7) some as large as $200\text{ }\mu\text{m}$ in diameter. However, as the MBM particle size was reduced the number

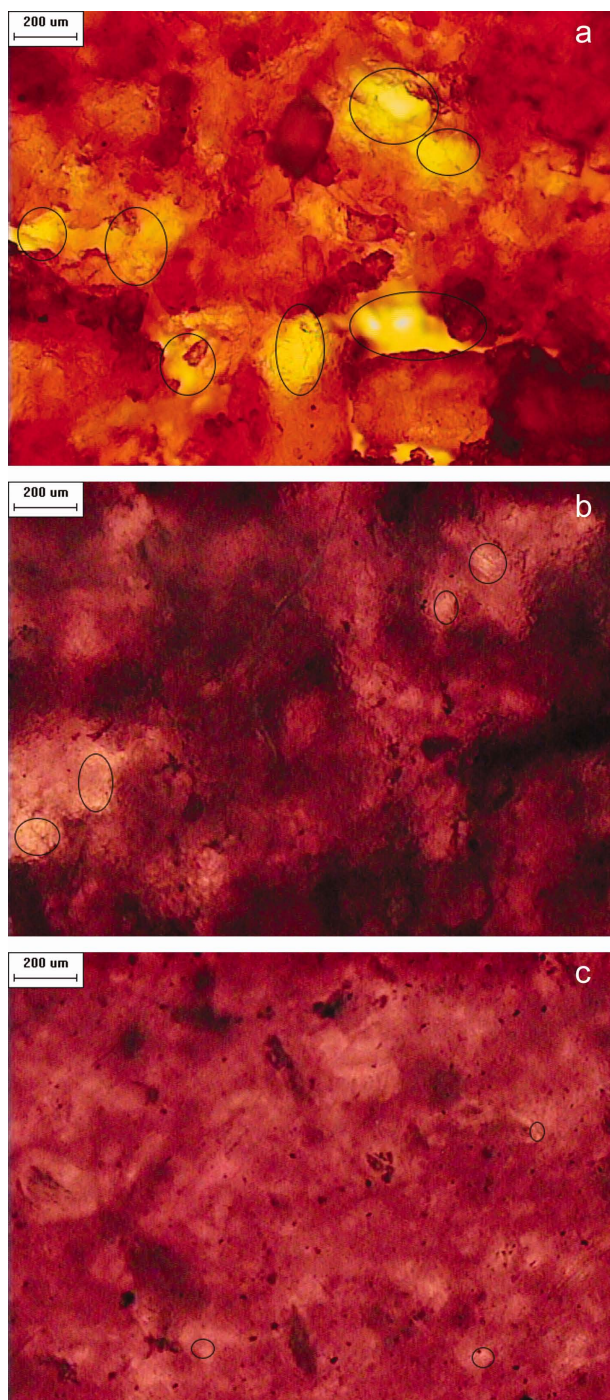


Figure 2. Transmitted light micrographs of MBM-glycerol (70–30) sheets 0.6 mm thick and made from (a) as-received MBM, (b) milled, coarse MBM, and (c) milled, fine MBM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and size of holes reduced such that sheets from fine MBM did not show regions of significant intense light transmission. It is evident that as the MBM particle size became smaller, uniform and better consolidated sheets were formed. Thus, the fine grade of milled MBM was used throughout most of the remainder of the study.

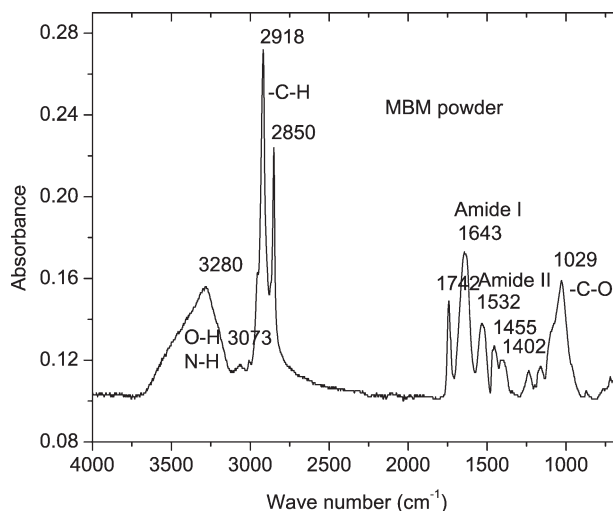


Figure 3. FTIR spectrum of MBM powder showing the amide I and amide II peaks and other peaks.

Another processing variable that affected sheet quality was the environmental humidity during processing. It was observed that, despite the raw MBM having similar initial moisture content of 6.9% (dry basis), different plasticized blends were obtained in different humidity conditions during compounding. The raw MBM powder compounded at a relative humidity (RH) of 30% produced powdery material incapable of producing sheets. At a RH of about 50%, rubbery chunks were produced, because of the denaturation effect of moisture. This is consistent with the observations reported in prior literature studies that showed an optimal amount of water is needed, in addition to heat for film formation from proteins.¹⁸ However, it was observed that high humidity levels (greater than 65%) results in excessive denaturation, which led to a sticky material that is not suitable for sheet formation. Thus, sheet formation from MBM protein by thermoplastic processing requires attention to plasticizer content, particle size, and environmental humidity. However, the well-consolidated sheets of fine MBM plasticized with 30% glycerol still possessed a tensile strength of only 0.8 ± 0.1 MPa. This is much lower than tensile strength displayed by synthetic polymers like LLDPE (~ 30 MPa).

In an attempt to improve mechanical properties, enhancement of molecular interactions using CH as a chemical modifier was investigated next. FTIR analysis was used to analyze the change in chemical structure of sheets with increasing CH content. The FTIR spectrum of milled MBM is shown first in Figure 3. MBM, being a multicomponent material, shows numerous peaks consistent with the results from prior literature studies.²⁶ It has a broadened peak at 3280 cm^{-1} because of the hydrophilic nature of MBM; the peak is attributed to O–H stretching from the moisture content of MBM. In the same region, there is an overlap of N–H stretching from proteins as well. The intense peaks at 2918 and 2850 cm^{-1} are because of C–H stretching. The peaks at 1455 and 1402 cm^{-1} are also because of C–H deformations. The protein component of MBM is shown by the 1643 cm^{-1} peak, which represents the amide I band (C=O) stretching in the protein secondary structure. The

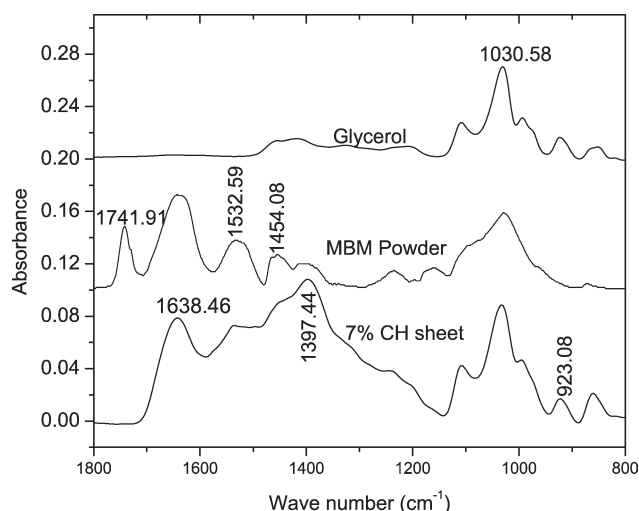


Figure 4. FTIR spectra of glycerol, MBM powder, and 7 wt % MBM sheet.

1532 cm^{-1} peak is the amide II band because of N–H bending and C–N stretching. The fat portion of MBM is represented by C=O vibration peak at 1742 cm^{-1} and C–O vibration peak at 1029 cm^{-1} from ester linkage of glycerides.³²

Figure 4 displays the FT-IR spectra of a bioplastic sheet containing 7% CH; milled MBM powder and glycerol (plasticizer) are shown for comparison. It was observed that the consolidated sheet has a broadened amide II band; whereas the MBM powder has distinct amide I and amide II bands. The broadening is attributed to the interaction of various secondary protein structures (alpha and beta sheets) forming crosslinks with Ca^{2+} via negatively charged oxygen atoms from side residues like glutamate and aspartate.³³ MBM is reported to contain about 6% glutamic acid and 4% aspartic acid.³⁴ It is noted that the peak at 1742 cm^{-1} observed for MBM powder is absent for the processed sheet spectrum. This shows that at a CH concentration of 7 wt %, the fats present in MBM are hydrolyzed and saponified. Previous research on fat saponification has shown similar effects.³⁵ The saponification process results in formation of ionized carbonyls that do not absorb in the same region as the nonionized carbonyl of fats because of resonance effects of the formed carboxylate.³⁶ The distinct glycerol peaks between 950 and 1150 cm^{-1} still appear in the processed sheet, which confirm the plasticization presence of glycerol.

In Figure 5, FTIR spectra for sheets containing different CH composition (0, 3, 7, and 10 wt %) are displayed. A comparison of peaks between 1750 and 1100 cm^{-1} shows that at 3 wt % CH modification, no significant change in chemical structure is observed. Significant chemical changes are observed at CH concentration of 7 wt % or higher. Clearly, as explained previously, the 1740 cm^{-1} peak attributed to the C=O of fat glyceride disappears. Because there is increased interaction between the protein chains, broadening is observed in the amide II through amide III region. It can therefore be inferred that addition of CH content greater than 7 wt % increases protein chain interaction.

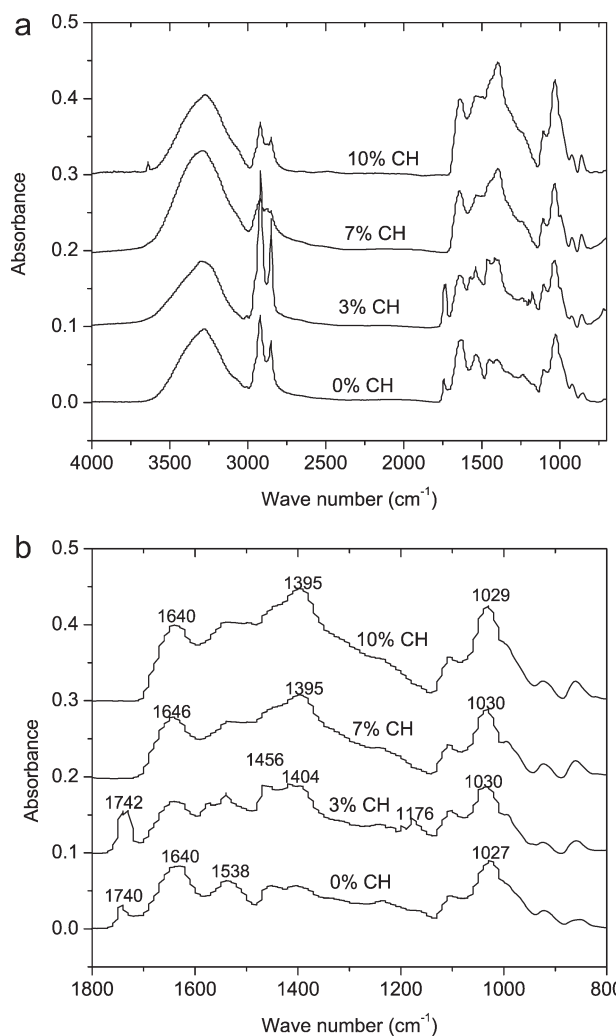


Figure 5. FTIR spectra comparing the molecular structure of MBM plastic sheets modified with different CH composition: (a) spectra over a wider range of wave numbers, and (b) zoomed-in spectra of fat and protein characteristic bands.

Mechanical properties

Table 1 displays the tensile modulus, strength, and strain to failure as a function of CH concentration of the plasticized sheets obtained from the fine grade of milled MBM (properties of coarse MBM are presented later for comparison purposes). As the CH concentration increased, the tensile strength initially decreased for 3 wt % CH modification to half the value for nonmodified sheets ($0.8 \pm 0.1\text{ MPa}$). However, for higher CH content, TS increased by a factor of about four, to $3.22 \pm 0.38\text{ MPa}$ for 7 wt % CH. Increase of CH to 10% resulted in sheets with TS ~ 5 times that of sheets with 0 wt % CH. Strain to failure generally decreased as the CH content was increased from 0 to 10 wt %. Sheets with 3 and 7 wt % CH, had their strain to failure decrease by about 40% while that of 10 wt % CH sheets, decreased by 75% compared to unmodified sheets. Similar to the tensile strength, tensile modulus (TM) of the sheets first decreased when 3 wt % CH was added, but increased by a factor of 3 and 8 when 7 and 10 wt % CH were, added respectively.

Table I. Comparison of Tensile Strength (TS), Strain to Failure, and Apparent Tensile Modulus (TM) of Sheets Made from Fine MBM with Different CH Contents

Composition	TS (MPa)	Strain to failure (%)	Modulus (MPa)
0% CH	0.84 ± 0.10	8.90 ± 1.20	40.16 ± 2.90
3% CH	0.48 ± 0.06	4.95 ± 0.50	34.84 ± 2.23
7% CH	3.22 ± 0.38	6.52 ± 2.45	139.4 ± 20.10
10% CH	3.96 ± 0.55	2.10 ± 0.39	341 ± 50.78

Test samples were preconditioned in a 75 cm Hg vacuum at 50°C for 24 h (n = 5).

For comparison purposes, MBM sheets produced from coarse MBM and modified with 0, 3, 7, and 10 wt % CH were also tested, and found to have TS values of 0.62 ± 0.01 , 0.34 ± 0.02 , 1.65 ± 0.06 , and 2.3 ± 0.52 MPa, respectively. Corresponding values for MBM sheets from fine MBM were 0.84 ± 0.1 , 0.48 ± 0.06 , 3.22 ± 0.38 , 3.96 ± 0.55 , respectively. In general, sheets made from fine MBM had higher TS than those from coarse MBM. For sheets modified with 7 wt % CH, the fine MBM sheets had a tensile strength of 3.2 MPa and an apparent modulus of 140 MPa, which were twice those of the sheets made from coarse

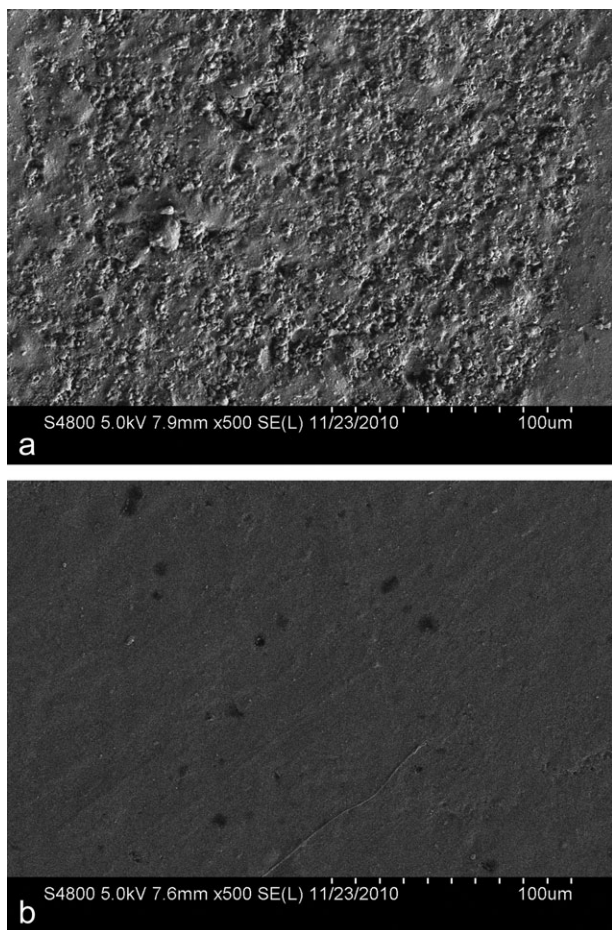


Figure 6. SEM plane surface images of MBM sheets with 7 wt % CH: (a) sheet from coarse MBM, and (b) sheet from fine MBM.

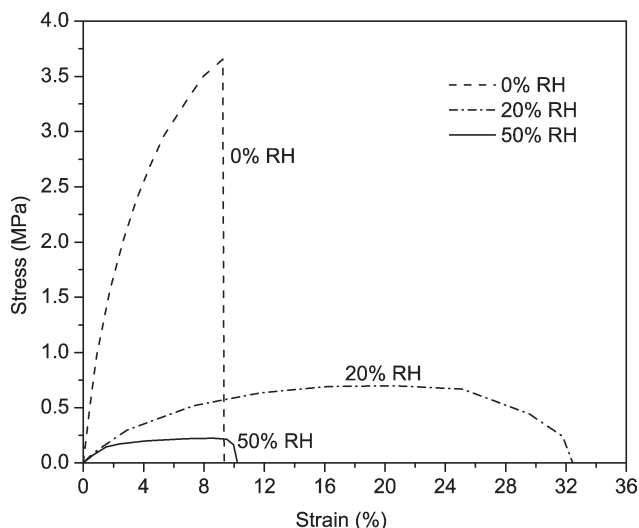


Figure 7. Stress–strain plot showing the effect of environment humidity on the tensile properties of 7 wt % CH modified sheets from fine MBM at 25°C. Test sample were preconditioned for 24 h at each humidity level.

MBM. The strain to failure was found to be about half (6.5%) that of the sheet made with the coarse MBM. Figure 6 displays the corresponding SEM micrographs illustrating the difference in surface microstructure of the CH modified sheets from fine and coarse MBM. Higher TS and TM are observed with smaller particle MBM because of better consolidation through increased protein chain interactions. On the other hand, coarse MBM has an effect close to that observed in discontinuous fillers that typically reduce tensile strength of composites.³⁷

Figure 7 presents stress–strain plots for 7 wt % CH modified MBM sheet showing the effect of environment humidity on the mechanical properties. The samples were preconditioned at 0%, 20%, and 50% RH. At 0% RH, the samples showed glassy behavior with a high modulus of 140 MPa and low strain to break of about 10%. When the RH was increased to 20%, the sheets demonstrated a rubbery behavior with the modulus decreasing by almost an order of magnitude to 17 MPa, whereas the elongation to break increased by a factor of 3 (to 30%). Increase in the RH to 50% decreased the modulus further to 13 MPa and also decreased the strain to failure to values close to those of samples conditioned at ~0% RH.

At very low humidity levels, the intermolecular bonds of the sheets are strong and lead to high TM and TS but lower strain to failure. Because MBM protein and glycerol are hydrophilic, moisture is readily absorbed by the sheets. As water molecules diffuse within the protein chains, they weaken the protein bonds and crosslinks, which lead to lower TM and TS, whereas the strain to failure increases. However, if excessive moisture is absorbed, the protein chain network is largely destroyed resulting in a decline of the strain as well. Therefore, mechanical properties of MBM sheets can be tailored by adjusting moisture content depending on the desired application.

Figures 8(a,b) display dynamic tensile moduli as a function of frequency for 0, 3, 7, and 10 wt % CH modified MBM (fine, milled). For all compositions, as the frequency increased, the

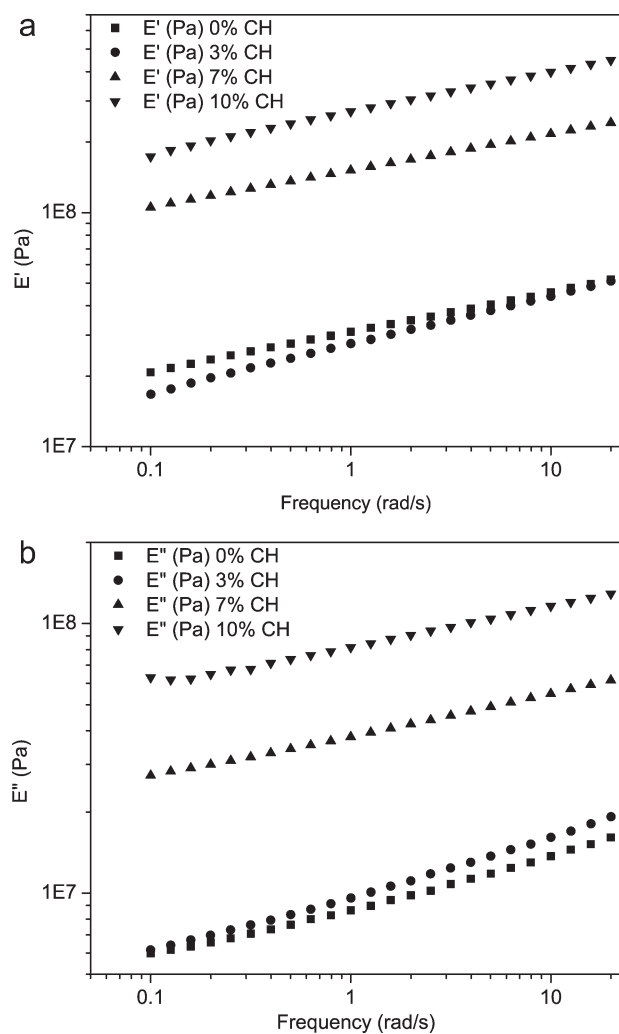


Figure 8. Plots of dynamic tensile moduli as a function of frequency for 0%, 3%, 7%, and 10% CH modified fine-MBM sheets: (a) storage modulus (E') and (b) loss modulus (E'').

dynamic TM increased and solid behavior was observed over the entire frequency range with the storage modulus being an order of ~ 3 higher than the loss modulus. From Figure 8(a), as observed with the static modulus, addition of CH of 3 wt % resulted in a lower dynamic TM. Further increase of CH content to 7 and 10 wt % resulted in an increase in the dynamic TM of 5-fold and 10-fold, respectively. These observations are consistent with the literature studies where the presence of metal ions like Ca^{2+} ions resulted in increased modulus of biological gels like alginate.²⁰

Figures 9(a,b) display the dynamic TM of 0%, 3%, 7%, and 10% CH modified fine-MBM sheets as a function of test temperature. From 25°C to 50°C, as expected, all the samples showed a decrease in the dynamic TM. However, solid behavior was maintained over the given temperature range with the dynamic storage modulus (E') remaining about three times higher than the loss modulus (E''). Samples containing 0 and 3 wt % CH had the modulus decrease by approximately a factor of 4; whereas sheets containing 7 and 10 wt % CH had a

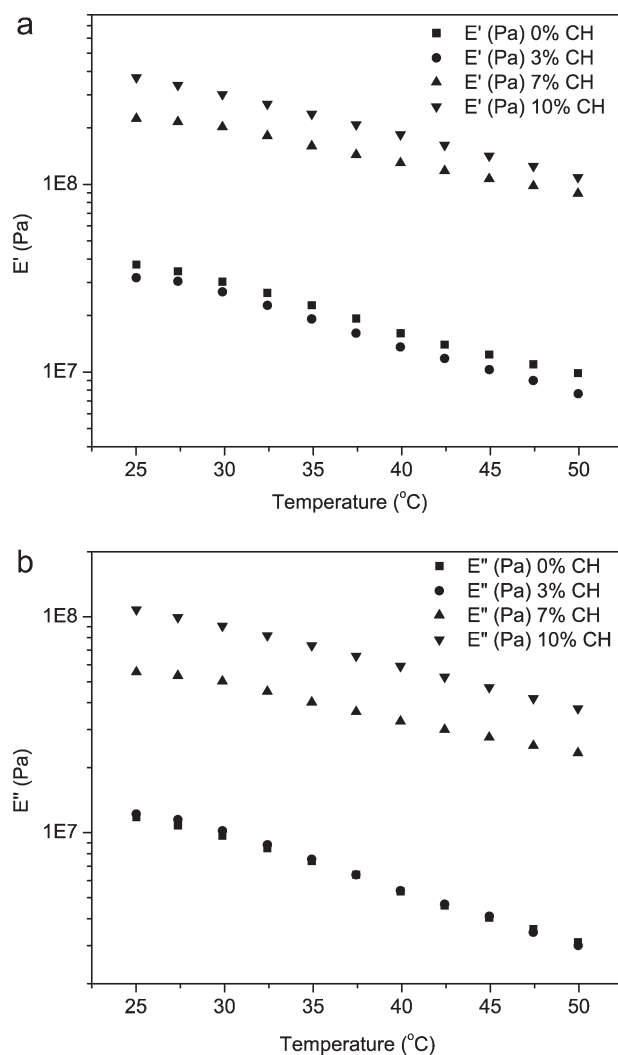


Figure 9. Plots of dynamic tensile moduli as a function of temperature for 0%, 3%, 7% and 10 wt % CH modified fine-MBM sheets: (a) dynamic storage modulus (E'), and (b) dynamic loss modulus (E'').

decrease of approximately a factor of 2 and 3, respectively. MBM sheets with 3 wt % CH content showed a lower dynamic TM than those without CH over the entire test temperature range, whereas sheets containing 7 and 10 wt % had significantly higher dynamic TM in comparison with that for samples containing no CH. At the highest test temperature of 50°C, for samples containing 7 and 10 wt % CH, dynamic TM was approximately an order of magnitude higher than that of unmodified samples. Sheets modified with CH content greater than 7 wt % had significantly higher thermal stability than those with no CH.

The increase in TS and TM of the sheets is primarily attributed to two factors: (i) enhanced denaturation that results in more extended conformations hence more structuring, and (ii) the increased interaction of protein chains through crosslinks with calcium ions via negatively charged oxygen atoms from side residues like glutamate and aspartate. The crosslinks may also be from uncharged oxygen atoms of the main chain carbonyl groups with side chain oxygen atoms from glutamine and

asparagine similar to that shown in prior literature studies.³³ The FTIR results discussed in the previous section demonstrated this effect of CH on the chemical structure for CH content greater than 7 wt %. Similar observations were reported in literature studies where soy films from calcium chloride treated solution had TS twice that of films from the untreated solution.²¹

CONCLUSIONS

MBM was successfully processed by thermal compaction into bioplastic sheets using glycerol plasticizer. The processability of MBM was influenced by MBM particle size and environmental humidity. Well-consolidated sheets were produced from fine MBM at ~50% RH, but these sheets possess poor mechanical properties (about 2% of the TS of a synthetic polymer like LLDPE). Chemical modification with CH (7–10 wt %) led to an increase in tensile strength and tensile modulus of MBM sheets by a factor of 4 to 8. The mechanical properties of the sheets were also affected by MBM particle size and the environmental humidity. The samples from fine MBM had a TS of 4 MPa, which was twice that of samples from coarse MBM. The FTIR spectroscopic analysis demonstrated an increase in protein interaction in samples with CH content greater than 7 wt % as inferred from the broadening of the amide II region (1500–1560 cm⁻¹). The improvements of the mechanical properties are attributed to crosslinking effect of calcium ions between the negatively charged oxygen atoms of protein side residues.

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