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Water Plasticization of Extruded Material Made from Meat and Bone Meal and Sodium Caseinate

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Meat and bone meal (MBM) is a high protein agricultural commodity that currently has few applications other than as an animal feed. Unmodified MBM has poor functional properties, due to its low solubility. Our results from pilot plant trials demonstrate that MBM can be extrusion-processed along with sodium caseinate to produce a useful plastic material. We developed this material for use as a dog chew toy. For this application, elastic modulus (stiffness) is a key characteristic. Our results detail the relationship between ambient relative humidity and equilibrium moisture content (MC) in the material. The influence of MC on the glass transition temperature and elastic modulus reflects the plasticization of this material by water. On the basis of a comparison to a commercially available dog chew, the range of stiffness achievable with our material, 0.25–2.50 GPa, encompasses the values appropriate for a dog chew. Our results show that a particular desired stiffness can be maintained by applying an edible moisture barrier to the surface of the material.

KEYWORDS: Meat and bone meal; casein; moisture sorption isotherm; bio-based material; extrusion; texture; glass transition temperature; dog chew; moisture barrier; stiffness

INTRODUCTION

Meat and bone meal (MBM), a high protein byproduct of the meat-rendering industry, is primarily used in formulating animal feed (1, 2). The outbreak of bovine spongiform encephalopathy in Europe has led to new laws proscribing the use of MBM in ruminant feed in the United States and in any farm animal feed in the European Union (3–5). A looming glut of MBM has spurred the search for alternative uses.

Unmodified MBM has poor functional properties due to its low solubility. This precludes many alternative applications, such as films, gels, adhesives, and foams, which have been developed for other high protein commodities, such as soy protein isolate (6–8). As a consequence, only very low value alternative uses for MBM, including fuel and fertilizer use, have been developed at this time (4, 9). These alternative uses currently consume an insignificant fraction of the U.S. MBM production.

The present study demonstrates that low cost, poorly functional MBM can be extrusion-processed along with relatively high cost, highly functional sodium caseinate to produce a useful plastic material. This plastic material was developed for use as a dog chew. Dog chews are edible toys that dogs slowly gnaw apart over a period of hours or days. For this application, we anticipate that the stiffness of the material will be the primary characteristic that will determine dogs' acceptance of the material. A material that is not stiff enough will be too easily

deformed by chewing action and rapidly consumed by the dog; an excessively stiff material will not be deformed significantly by chewing action and will likely be rejected as a chew toy.

Our results show that the extruded material has characteristics consistent with those of an amorphous hydrophilic polymer. Water is an effective plasticizer of this material, and the water content of the material can be manipulated to produce a range of stiffness, including a stiffness appropriate for a dog chew toy.

MATERIALS AND METHODS

MBM was received from the Moyer Packing Company (Souderton, PA) and milled along with crushed dry ice in a Wiley mill to pass through a screen with 1 mm openings. Sodium caseinate (Alanate 110) was purchased from New Zealand Milk Products (Santa Rosa, CA). A 1:1 mixture of the dry ingredients was blended in a V-blender for 15 min.

Extrusion. The blends were fed into the extruder using a series 6300, type 35 twin-screw volumetric feeder (K-tron Corp., Pitman, NJ) at a constant setting of 700 rpm, yielding a feed rate of 42.1 g/min. The blends were extruded from a ZSK30 twin-screw extruder (Werner & Pfleiderer Company, Ramsey, NJ) with nine individual barrel sections, each with a separate temperature control. The temperatures of the barrel sections, from material entry to exit, were 35, 35, 55, 60, 75, 85, 90, 85, and 80 °C. The extruder was set up with a low shear screw configuration, running at a constant 100 rpm. The die plate was set with a 3.18 mm diameter circular orifice. Water was added using two electromagnetic dosing pumps (Milton Roy, Acton, MA) with the pump settings (stroke length/frequency) set at 40/20 and 40/10 corresponding to 33 mL/min added water. The extruded material had an exit temperature of 68 °C; long rods of the material were collected on trays to cool and harden.

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Preparation of Test Specimens. Specimens for mechanical property testing were prepared by cutting the extruded rods into cylinders 23 mm in height and 6–8 mm diameter. A fine-toothed miter saw was used to ensure that the ends were cut normal to the axis of the cylinder. Specimens for moisture sorption and thermal analysis were prepared by cutting 1 mm wafers from the extruded rods using the miter saw. Thermal analysis specimens were further reduced in size by using a cork borer to cut 4 mm diameter disks from the wafers. Specimens were handled with clean gloves and tweezers to avoid contamination. Each type of specimen was adjusted to a range of moisture contents (MC) by storing it in a chamber of constant relative humidity (RH) until the mass of the specimen was constant for 2 weeks. The equilibration chambers were set up according to ASTM E 104-02 (10) and consisted of small, airtight jars containing saturated salt solutions and plastic stands to hold the sample above the salt solution. The solutions of LiCl, CH₃COOK, MgCl₂, K₂CO₃, NaBr, KI, NaCl, and KCl stored at 23 °C (± 1.5 °C) equilibrate with the headspace air resulting in a RH of 11.6, 22.7, 32.9, 43.2, 58.2, 69.3, 75.4, and 84.6%, respectively. A RH of 0% was achieved by partially filling a jar with indicating Drierite (W. A. Hammond Drierite Co., Xenia, OH) rather than a salt solution. The specimens were stored in the jars until just before use.

Moisture Sorption Isotherm. In moisture absorption experiments, specimens were prepared as described above, except that they were dried in a 70 °C vacuum oven for 36 h and accurately weighed before placing them in the constant RH chambers. In moisture desorption experiments, the specimens were dried in a vacuum oven for 36 h, accurately weighed, placed in a chamber with 100% RH at 23 °C for 66 h, and then finally transferred to the constant RH chambers.

The specimens were removed from the chambers and weighed three times per week. Equilibration was allowed to continue until the mass of a particular specimen was constant at three consecutive time points. Moisture absorption and desorption were determined in quadruplicate.

Thermal Analysis. Test specimens were weighed and hermetically sealed in aluminum differential scanning calorimetry (DSC) pans. The glass transition temperature (T_g) was determined using a Pyris 1 DSC (Perkin-Elmer, Wellesley, MA). The specimens were scanned twice to eliminate the hysteresis effect due to thermal relaxation. The initial scanning raised the specimen temperature from 0 to 160 °C at a rate of 20 °C/min, followed by cooling to -70 °C at 200 °C/min, a 2 min hold, and finally a second scan from -70 to 160 °C at a rate of 20 °C/min. The T_g was identified by locating a step change in the heat capacity in the thermogram trace from the second heating. The value of the T_g was determined as the temperature of a peak in the derivative of the trace. Four to eight specimens were analyzed at each MC. The data on the MC of the specimens at each RH were obtained from the moisture sorption isotherm.

Mechanical Properties. The mechanical properties were measured in compression, using a Sintech/2GT material testing system (MTS, Minneapolis, MN). The modulus of elasticity was determined according to the ASTM D 695-02 (11) method. The cross-head speed was 1.3 mm/min, and five replicates were tested for each experimental condition. The data on the MC of the specimens at each RH were obtained from the moisture sorption isotherm.

Moisture Barrier. In the final experiments only, the test specimens were submerged in molten (50 °C) edible beef tallow (T. R. R. Industries, Chicago, IL) for 1 s and then submerged in liquid nitrogen for 2 s to solidify the tallow coating. The process was repeated to apply a second layer of tallow to the specimens.

Data Analysis. All data analysis was performed using Analyse-It (Analyse-It Software, Ltd., Leeds, England).

RESULTS AND DISCUSSION

The moisture sorption isotherm in **Figure 1** details the nonlinear relationship between the MC of the extruded material and its water activity. The overall shape of the isotherm is intermediate between the sigmoidal shape typically produced by amorphous solids and the “exponential” shape typically produced by crystalline solids (12). Hysteresis between the

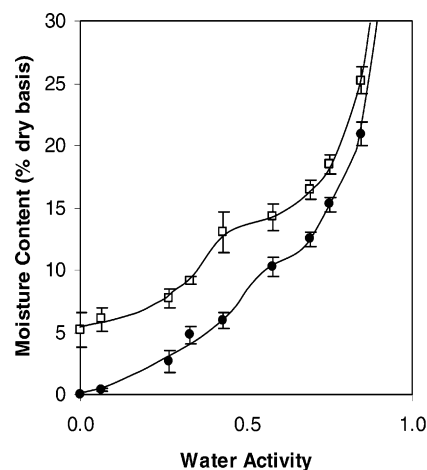


Figure 1. Moisture absorption (●) and desorption (□) isotherms for extruded material at 23 °C (± 1.5 °C) with four replications at each water activity; error bars are ± 1 SD.

absorption and desorption isotherms occurs for a variety of reasons and is routinely observed with food and other bio-based materials (12, 13).

This relationship was used to adjust the MC of the extruded material for further experiments. By incubating the samples at a variety of RH and allowing adequate time for equilibration, the material's MC could be set precisely. While most samples equilibrated within a few weeks, the cylinders for mechanical testing took up to 9 weeks to equilibrate.

DSC scans of the extruded material contain a step change in heat capacity, which is consistent with the glass transition of an amorphous solid. A typical thermogram is shown in **Figure 2**. The higher the MC, the less distinctly this feature appeared. This is consistent with a known phenomenon; at higher plasticizer contents, amorphous solids go through the glass transition at an increasingly wide range of temperatures, leading to a less distinct transition (14).

Water has the defining effect of a plasticizer on an amorphous solid, lowering the T_g . In the MC range of 7.5–15% [dry basis (db)], an increasing MC produces material with a lower T_g (see **Figure 3**). Other proteins have been reported to behave as amorphous solids plasticized by water, including the 7S and 11S soy proteins (14), wheat gluten (15), and gelatin (16).

High moisture specimens (MC $\geq 15\%$ db) displayed relatively high ductility; that is, they can undergo large strains before failing (see **Figure 4**). These samples displayed a yield stress (the stress at which the strain increases without an increase in applied stress—not shown in figure) after which the test was aborted.

The stress applied to test specimens was limited by the testing equipment used; for lower moisture samples (MC $< 15\%$ db), this limit was not high enough stress to cause them to yield or fracture. The lower moisture samples can be expected to be glassier, based on the results of the DSC studies. Glassy materials are brittle (the opposite of ductile—they fail with a low amount of strain), and their fractured surfaces often have very sharp edges. The sharp edges of fractured glassy material could potentially injure a dog that is chewing on the material; ideally, a dog chew material should be somewhat rubbery to reduce this risk.

In the range of 7.5–15% moisture (db), the modulus of elasticity decreases almost linearly; below 7.5%, further changes in modulus are not apparent (see **Figure 5**). These results closely parallel the decrease in T_g in response to the increasing MC (see **Figure 3**). The range of stiffness exhibited by the extruded

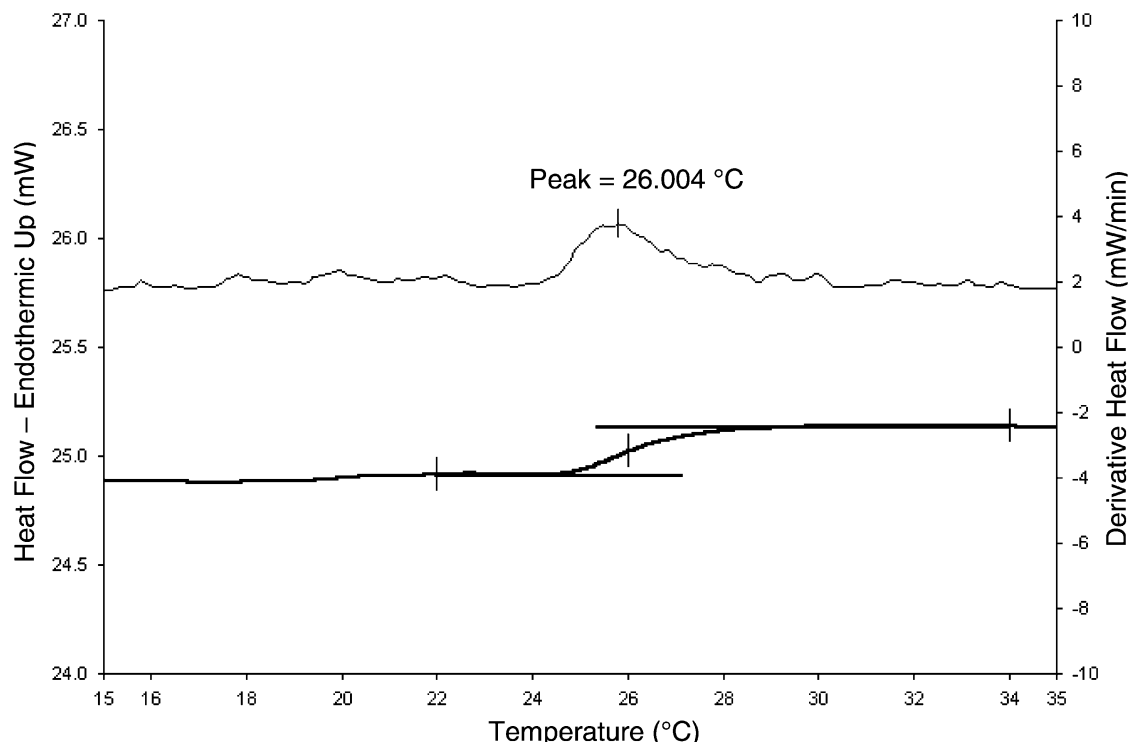


Figure 2. DSC determination of glass transition temperature in extruded material. The lower trace (left ordinate) is the actual heat flow during the second heating of the material; the upper trace (right ordinate) is the derivative of heat flow.

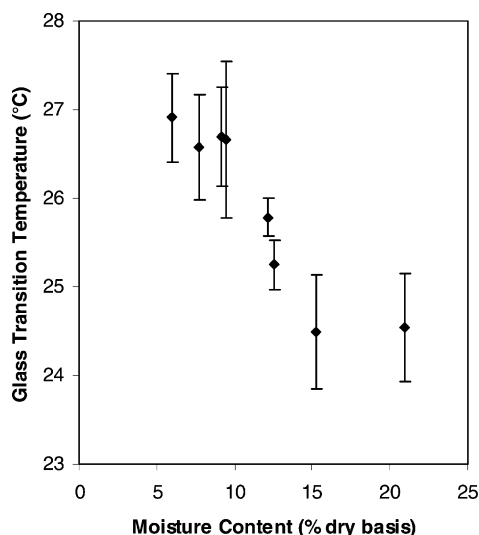


Figure 3. Effect of MC on glass transition temperature. Error bars are \pm one SD; there were 4–7 replicates at each MC.

material encompasses values reported for widely used petrochemical polymers, including 1.0–2.1 GPa for poly(propylene) and 2.3–4.1 GPa for poly(vinyl chloride), using the same method as the present work (17).

A wide variety of commercial dog chews are available, and these products have a wide range of stiffness. We selected a particular commercial dog chew (Dentley's Chewrite rawhide sticks, Pacific Coast Distributing, Phoenix, AZ) to compare to the extruded material. Mechanical testing of the commercial bones gave a modulus of elasticity of 687.1 MPa (SD = 151.5 MPa, $n = 7$). The previous results (Figure 5) demonstrate that the extruded material has roughly the same stiffness as the commercial bone when its MC is 15.25% (db). The MC of the extruded material can be easily manipulated in production, but after production, the MC will change depending on the RH of the surrounding air. One way to prevent a change in the MC is

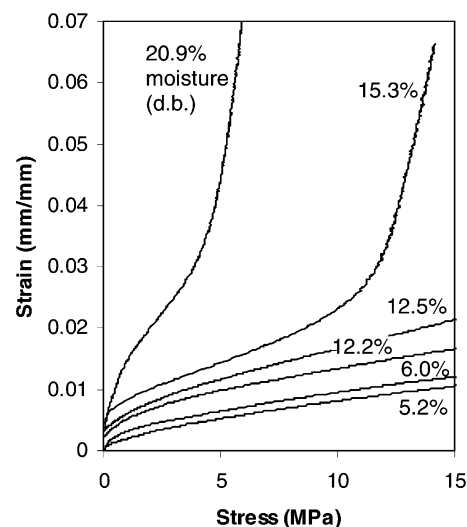


Figure 4. Deformation of extruded cylinders compressed axially. The lowest curve represents the driest material, and the curves above it represent materials with increasing MCs, in order.

to apply an edible moisture barrier to the surface of the product (18). We created a moisture barrier by dipping the extruded material in molten edible beef tallow. The extruded material equilibrated to a MC of 15.28% is coated with tallow and placed in a desiccator; an identical extruded material, not coated with tallow, is also placed in the desiccator. The effectiveness of tallow as a moisture barrier is illustrated in Figure 6. We observed a much lower rate of mass change in the coated material, as compared to the uncoated material, indicating a more stable MC in the coated material, when in a nonequilibrium environment. Ideally, the moisture barrier would have been even more effective in preventing water loss; we believe that the barrier suffered from imperfections where it was handled with tweezers, allowing some water to escape. The stiffness of the material after storage for 48 h in the desiccator was 1338 MPa

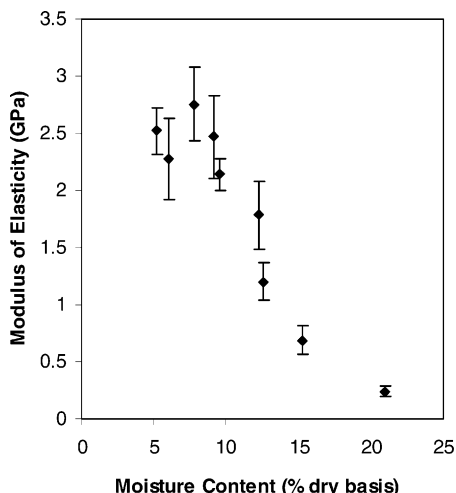


Figure 5. Effect of MC on stiffness of extruded material. Experiment conducted at 22 °C; $n = 5$; error bars are \pm one SD.

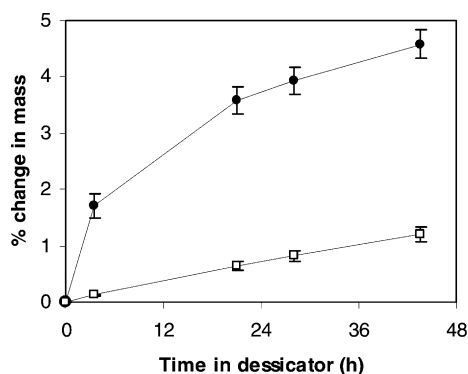


Figure 6. Moisture loss from tallow-coated extruded material (□) and uncoated material (●) in a drying environment. Error bars are \pm one SD; there were five replicates at each data point.

(SD = 109 MPa, $n = 5$), which is significantly higher than the commercial chew that we tested.

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