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Water adsorption characteristics of extruded blends of corn gluten meal and distillers dried grains with solubles

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ABSTRACT

Corn-based ethanol has experienced exponential growth during the last decade. As a consequence, the production of byproduct corn protein meals, in the form of DDGS (distillers dried grains with solubles) and CGM (corn gluten meal) has grown as well. These materials are used as livestock feed. Extrusion processing is one method of converting these materials into other value-added materials, bioplastics, or other industrial precursors. The objectives of this study were to extrude blends of these materials, then examine dynamic and equilibrium relationships of extruded products with water. Blends consisted of DDGS:CGM ratios of 0, 33, 50, 66, and 100%. After processing, extrudates were placed in sealed chambers with headspace relative humidities ranging from 10% to 90%. Moisture contents were monitored over time. All samples achieved moisture equilibrium in less than three weeks. As with all biological materials, the extruded corn protein blends exhibited sorption behavior, the magnitude of which varied according to blend ratio. EMC values ranged from approximately 0% to nearly 50%, depending upon the humidity level and fiber:protein ratio. Nonlinear regression was successfully used to model the effects of relative humidity and blend ratio on the equilibrium moisture contents, with a coefficient of determination of ~99%. Future work should aim to characterize the mechanical properties of these blends to assess their suitability as either bioplastic feedstocks or pelletized animal feeds.

1. Introduction

Petrochemical polymers have become ubiquitous for their highly functional properties and durability. Unfortunately, they also create an enormous environmental burdens. Motivations behind sustained research in reducing dependence on polymers from petrochemical sources are similar to those in energy research; a decreasing fossil fuel supply with a corresponding price increase and a widespread awareness of sustainability (Gandini, 2008).

There are two primary ways to address the energy challenge: reduce energy consumption and/or develop alternative methods of energy production. Biofuels are renewable sources of domestic energy, and are a promising alternative. One of the most frequently used materials for energy production is corn starch (Liu and Rosentrater, 2011). Fuel ethanol production from corn can be accomplished very efficiently and at a relatively low cost. Two main techniques are used to commercially produce ethanol: wet milling and dry grind processing. The wet milling process consists of steeping the raw corn to moisten and soften the kernels, milling, and then separating the kernel components through various fractionation processes. The primary end products are corn starch, corn oil, and ethanol (Johnson and May, 2003). Additional end-products include corn gluten feed (CGF), corn gluten meal (CGM), corn germ meal, and condensed fermented corn extractives (Loy and Wright, 2003). Dry grind processing, on the other hand, has become the primary method for ethanol production in the U.S., and uses the entire corn kernel (Bothast and Schlicher, 2005). After milling, the resulting flour is combined with water, enzymes, and other additives and is then cooked and fermented. Ethanol is extracted using distillation as well as

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centrifugation to remove residual non-fermentable corn kernel components, water, and carbon dioxide. The non-fermentable materials are usually combined, dried and sold as 'distillers dried grains with solubles', or DDGS.

The potential use of agro-polymers in the plastics industry has long been recognized. Agro-polymers are extracted from either plants or animals, such as those described above. Some of the polymers in this family can be processed directly into thermoplastic materials; however, most requires chemical modification. A further benefit is that these polymers are often by-products of other agricultural activities. Common characteristics of agro-polymers are their hydrophilicity, fast degradation rate and sometimes unsatisfactory mechanical properties, particularly in wet environments (Verbeek and Bier, 2011). These polymers can be considered an innovative and sustainable approach to reduce reliance on petrochemical polymers (Chivrac et al., 2009). The main technological challenge is to successfully modify the properties of these materials to account for deficiencies such as brittleness, water sensitivity and low strength.

Petroleum-based materials could potentially be replaced with renewable and biodegradable materials such as polysaccharides or proteins (Verbeek and Bier, 2011). As a result, finding new uses for agricultural commodities has become an important area of research. Although bioplastics may appear to be a perfect solution to these problems, bioplastics also have some drawbacks; most importantly the perceived competition with food production. As a result, attention is shifting to second generation bioplastics manufactured from non-potential food sources. However, one of the challenges for bioplastics is to be successfully integrated into common synthetic plastic processing routes, such as extrusion and injection moulding.

In previous work it has been shown that CGM can be used to produce thermoplastic materials (Pickering et al., 2012). CGM has a high protein content, which makes it more suitable as a thermoplastic precursor than DDGS. DDGS has a high fiber content and a low protein content compared to CGM; however, it is considerably cheaper and produced at much higher quantities than CGM. This is a direct result of the growth of the corn-based fuel ethanol industry during the last decade. Now more than 30 million metric tons are produced annually in the U.S. alone.

DDGS and CGM, as with other organic and biological materials, are hygroscopic in nature, and gain or lose moisture when they are exposed to various humidity conditions. Because gaining water (adsorption) or losing water (desorption) is a thermodynamic process, both ambient temperature and humidity dictate the rate of sorption. Sorption is also affected by the biological matrix, as thermodynamically-bound water is difficult to remove, while free (unbound) water readily sorbs. Sorption is a dynamic process, driven primarily by the moisture gradient, and continues until the water in the material is in equilibrium with the surrounding environment.

While sorption can be beneficial at times, it can also lead to unanticipated physical and chemical changes in the material, as well as negative impacts on subsequent processability. Each material absorbs moisture at different rates under different temperature and humidity conditions, but combinations of DDGS and CGM have not yet been examined, nor have these relationships been determined for these materials after processing into biopolymers.

Thus the overall objectives of this research were to develop corn protein-based bioplastics by replacing portions of CGM with DDGS. Processability, morphology, and thermal properties of these blends were evaluated; these results have been published in another work (Rosentrater and Verbeek, 2012). This portion of the study specifically focused on dynamic and equilibrium relationships of these extruded polymers with water.

2. Materials and methods

2.1. *Sample collection and protein modification*

Protein meals for this study consisted of distillers dried grains with solubles (DDGS) and corn gluten meal (CGM). DDGS was obtained from a commercial ethanol plant (VeraSun, Aurora, SD, USA), and had the lipids removed via solvent extraction (Saunders and Rosentrater, 2009). CGM was obtained from Consumers Supply Distributing (Sioux City, IA, USA). All materials were stored in sealed plastic buckets at room temperature (25 °C ± 1 °C) until needed. Proximate composition (Table 1) of each was determined by ServiTech Laboratories (Hastings, NE, USA). The CGM had approximately twice as much protein as the DDGS, while the DDGS contained almost 10 times as much fiber as the CGM.

Table 1 – Proximate composition of the raw protein sources used in the study.

Component	CGM	DDGS
Dry matter (%)	90.8	98.0
Crude protein (% db)	67.4	34.0
Crude lipid (% db)	2.2	2.7
Carbohydrate (% db) (by difference)	28.1	58.5
Neutral detergent fiber (% db)	5.7	50.1
Starch (% db)	15.0	5.0
Ash (% db)	2.3	4.8

Prior to extrusion processing, the proteins in the DDGS and the CGM were modified by combining 100 parts protein meal, 50 parts water, and 10 parts urea (i.e., 10 g urea dissolved in 50 g water per 100 g of protein meal). Materials were thoroughly mixed for 30 min in a rotating drum mixer, sealed in plastic containers, then left to equilibrate for 24 h prior to extrusion processing. Immediately before extrusion, five blends were formulated (on a mass basis) to consist of DDGS:CGM ratios of 0:100, 33:66, 50:50, 66:33, and 100:0. These blending ratios resulted in NDF:protein ratios of 0.08, 0.55, 0.78, 1.01, 1.47, respectively.

2.2. *Extrusion processing*

After protein modification, the blends were extruded using a single screw autogenous (i.e., heat was not added externally; rather all heat was generated due to friction alone) extruder (Rietz, Extructor, Bepex International LLC, Minneapolis, MN, USA) to produce extruded biopolymers. The die plate consisted of 6 orifices equally spaced, 2 mm diameter each, with a total opening area of 18.85 mm^2. The extruder had a split barrel with three sections; the front (i.e., die) section was fitted with two thermocouples, with one placed at the entry to the section and the second placed near the die exit. A power meter (HIOKI 3196, HIOKI E.E. Corporation, Nagano, Japan) was used to continuously record power consumption. The input feed rate was set ensure steady state operation of the extruder, and was approximately ∼15 kg/h. Extrusions were carried out in duplicate for each blend combination (i.e., $n = 2$ for each treatment), for a total of 10 extrusion runs, following a completely randomized run order.

2.3. *Bio-based polymer analyses*

After extrusion processing, the biopolymers were cooled to room temperature then subjected to a variety of tests in order to examine the efficacy of conversion of the raw blends into continuous matrices as well as their resulting properties. These tests included mass density, thermal conductivity and diffusivity, color, optical microscopy, protein consolidation, transmission electron microscopy, and differential scanning calorimetry (to determine glass transition temperatures) and