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# Thermoplastic films from wheat proteins

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ABSTRACT

We show that the wheat proteins gluten, gliadin and glutenin can be compression molded into thermoplastic films with good tensile strength and water stability. Wheat gluten is inexpensive, abundantly available, derived from renewable resource and therefore widely studied for potential thermoplastic applications. However, previous reports on developing thermoplastics from wheat proteins have used high amounts of glycerol (30–40%) and low molding temperature (90–120 °C) resulting in thermoplastics with poor tensile properties and water stability making them unsuitable for most thermoplastic applications. In this research, we have developed thermoplastic films from wheat gluten, gliadin and glutenin using low glycerol concentration (15%) but high molding temperatures (100–150 °C). Our research shows that wheat protein films with good tensile strength (up to 6.7 MPa) and films that were stable in water can be obtained by choosing appropriate compression molding conditions. Among the wheat proteins, wheat gluten has high strength and elongation whereas glutenin with and without starch had high strength and modulus but relatively low elongation. Gliadin imparts good extensibility but decreased the water stability of gluten films. Gliadin films had strength of 2.2 MPa and good elongation of 46% but the films were unstable in water. Although the tensile properties of wheat protein films are inferior compared to synthetic thermoplastic films, the type of wheat proteins and compression molding conditions can be chosen to obtain wheat protein films with properties suitable for various applications.



## 1. Introduction

As coproducts of processing cereal crops for food and fuel, plant proteins such as wheat gluten and soyprotein are available in abundance, inexpensive and are derived from renewable resources (Hernandez-Izquierdo and Krochta, 2008; Cuq et al., 1998). However, there are limited industrial applications of the protein coproducts and most of the proteins currently have low value applications such as animal feed. Attempts have been made to use plant proteins to develop fibers, films, thermoplastics and also as matrix for composites (Reddy and Yang, 2007a,b, 2011a,b). Poor thermoplasticity, water resistance and brittleness are some of the main reasons for the limited use of plant protein based materials for industrial applications (Lagrain et al., 2010).

Due to their poor thermoplasticity, plasticizers are commonly used to melt proteins and develop thermoplastic products (Kunanopparat et al., 2008). Plasticizers are also used to improve the flexibility of plant protein based products. However, adding plasticizers decreases the strength and modulus and also makes the proteins more vulnerable to water (Gallestedt et al., 2004). Alternatively, chemical modifications have been considered to develop plant protein based bioplastics with good mechanical properties and water resistance (El-Wakil et al., 2007; Dicharry et al., 2006). Unfortunately, chemical modifications make the protein based bioplastics expensive compared to synthetic polymer based plastics and/or reduce the biodegradability of the proteins. Similarly, blending of plant proteins with synthetic polymers or reinforcing with natural fibers is a common approach to develop plant protein based products (Kunanopparat et al., 2008; Reddy and Yang, 2011a,b).

Wheat gluten has been widely used to develop films and other bioplastics (Dicharry et al., 2006; El-Wakil et al., 2007; Gallestedt et al., 2004; Kunanopparat et al., 2008; Zárate-Ramírez et al., 2011). Although wheat gluten films are mostly made using the dissolution method (solution casting), films developed by compression molding have better properties than solution cast films (Mangavel et al., 2004). Wheat gluten is inherently non-thermoplastic and therefore, plasticizers, chemical modifications or blending with thermoplastic polymers have been used to develop thermoplastics from wheat gluten (Sun et al., 2008a,b; Gallestedt et al., 2004).

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Glycerol (35%) plasticized wheat gluten was compression molded into dumbbell shaped thermoplastics at a relatively low temperature of 100 °C for 12 min (Sun et al., 2007). The effect of incorporating crosslinking agents such as aldehydes and L-cysteine on the morphology, moisture absorption, mechanical and tensile properties was studied. Thermoplastics with strength ranging from 2.0 to 3.5 MPa and elongation ranging from 125% to 200% were obtained when tested at 20 °C and 75% relative humidity. Aldehydes (glutaraldehyde and formaldehyde) induced crosslinking and improved tensile strength but lowered elongation and modulus of the wheat protein films (Sun et al., 2007). The transport and tensile properties of compression molded wheat gluten films were studied by Gallestedt et al. (2004). Wheat gluten was mixed with 25–45% glycerol and compression molded between 90 and 130 °C for 5–15 min to obtain thermoplastics with thickness of 0.5 mm. The fracture stress of the films ranged from 0.6 to 6.1 MPa, elongation ranged from 96% to 238% and modulus ranged from 0.2 to 8.1 MPa depending on the amount of glycerol and compression conditions used. Glycerol was found to have a more pronounced effect on the tensile properties than molding time or temperature (Gallestedt et al., 2004). In another report, it was found that compression temperature had significant effect on the tensile properties of wheat gluten films. Increasing molding temperature from 25 to 125 °C increased the tensile strength from 0.52 to 6.69 MPa, elongation from 174% up to 288% and modulus from 1.2 to 36 MPa (Sun et al., 2008a) when tested at 21 °C and 65% relative humidity. High temperatures were reported to promote intermolecular covalent bonding and improve the strength and modulus (Sun et al., 2008a).

Wheat gluten has also been used as a matrix for composites reinforced with natural fibers (Kunanopparat et al., 2008). Similarly, wheat gluten modified with urea and sodium hydroxide was used a binder for reed particle board (El-Wakil et al., 2007). Wheat gluten mixed with zein was used to develop composites by compression molding at room temperature (Kim, 2008). Composites with compressive strength up to 38 MPa and modulus of 2200 MPa were obtained by changing the ratio of gluten and zein. Wheat gluten modified with thiolated poly(vinyl alcohol) was reported to have 76% higher fracture strength and 80% higher elongation and 25% higher modulus compared to compression molded (150 °C, 10 min at 20,000 pounds) unmodified wheat gluten thermoplastics (Dicharry et al., 2006). Recently, water plasticized wheat gluten was used as a matrix material for jute fiber reinforced composites (Reddy and Yang, 2011b). It was found that wheat gluten as a binder provided better properties to the composites than polypropylene (Reddy and Yang, 2011b).

In addition to wheat gluten, gliadin and glutenin in wheat gluten have also been used to develop thermoplastics. Gliadin was mixed with glycerol (10–40%) and thermomolded at 120 ± 5 °C for 5 min at 15 MPa. Tensile strength ranging from 0.77 to 22 MPa, elongation at break from 8.5 to 301% and modulus from 0.03 to 4.58 MPa were obtained (Sun et al., 2008b). Glutenin rich wheat gluten obtained by removing gliadin was mixed with 40% glycerol and 2% reducing agent and compression molded into films at 125 °C for 10 min at 10 MPa. Tensile strength of the films varied from 1.5 to 1.9 MPa and elongation varied from 88 to 133% depending on the type of reducing agent used (Song and Zheng, 2008).

As seen from the above discussions, a wide range of conditions have been used to obtain thermoplastics from wheat proteins with varying properties. Since wheat gluten has poor thermoplasticity, plasticizers such as glycerol or chemical modifications are inevitably used to develop thermoplastics from wheat proteins. However, plasticizers such as glycerol commonly used to plasticize wheat proteins are hydrophilic, absorb considerbale amounts of water and therefore substantially decrease the mechanical properties and also reduce the water resistance of the thermoplastics (Pommet et al., 2005). For instance, wheat gluten films with 25% glycerol content absorbed 47.5% water compared to 73% for films with 40% glycerol. Similarly, the Young's modulus of wheat gluten-based materials decreased to 10.4 MPa from 34.7 MPa when the glycerol content was increased from 20 to 30% (Gallestedt et al., 2004). As seen from the literature discussed above, it is necessary to use plasticizers to develop thermoplastics from wheat gluten but wheat gluten thermoplastics containing plasticizers have poor mechanical properties (Kunanopparat et al., 2008). In addition, none of the above reports has reported the water-resistance of the wheat protein thermoplastics containing plasticizers. It is necessary to have good mechanical properties and water stability to obtain useful thermoplastics from wheat proteins.

In this research, we attempt to develop thermoplastics from wheat proteins with good strength and water stability using low levels of glycerol and by optimizing the compression molding conditions. The effect of type of wheat protein on the tensile properties and water resistance of the thermoplastics has also been studied.

## 2. Experimental

### 2.1. Materials

Commercially available wheat gluten (WhetPro 80) with approximately 80% proteins was supplied by Archer Daniel Midlands Company (Decatur, IL). Wheat gluten was used as received for the study. Ethanol and glycerol used were reagent grade chemicals purchased from VWR International. Gliadin was extracted from wheat gluten using 70% (v/v) ethanol. Gluten was mixed with 70% ethanol (4:1 ratio of ethanol to gluten) and stirred overnight at room temperature. The mixture was centrifuged at 8000 rpm for 10 min. The supernatant was collected and the ethanol was evaporated in a hood at room temperature to collect the gliadin. Residue obtained after removing gliadin was considered as glutenin with starch and used for the study. To study the effect of starch on properties of glutenin thermoplastics, gliadin free wheat gluten was treated with 1% amylase (Spirizyme, Novazymes), at 4:1 ratio of enzyme solution to gliadin free gluten at 50 °C for 48 h at pH 5.0 adjusted using sodium acetate buffer to obtain starch free glutenin. After the enzyme treatment, the proteins were centrifuged to remove dissolved starch and the proteins were thoroughly washed. The proteins obtained after removing starch were considered as pure glutenin and used for the study.

### 2.2. Developing thermoplastic films

Wheat proteins (gluten, gliadin, glutenin with starch and pure glutenin) were thoroughly mixed with 15% (w/w) glycerol by hand. The mixture was then spread evenly on aluminum foils and placed in a compression mold (Carver Press, Wabash, IN) at a pressure of 40,000 lbs. We first conducted initial trials to select the time for compression molding at a temperature of 150 °C. It was found that a compression time of 6 min for the wheat gluten, glutenin and pure glutenin and 2 min for gliadin films provided optimum tensile properties. Therefore, the effect of temperature (120–150 °C) was studied using a compression time of 6 min for the gluten, glutenin and glutenin films and 2 min for the gliadin films. After compression, the hot press was cooled by running cold water and the films formed were collected for further analyses.

We also prepared wheat gluten and gliadin films using conditions reported by other researchers for comparison. Wheat gluten was mixed with 35% glycerol and compression molded at 100 °C for 12 min (Sun et al., 2007) at 40,000 lbs. Gliadin films were compression molded at 120 °C for 15 min with 15% glycerol (Sun et al., 2008b) at 40,000 lbs.