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Preparation and properties of thermo-molded bioplastics of glutenin-rich fraction

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Abstract

The present work aims to prepare bioplastics from a glutenin-rich fraction; that is, the gluten residue insoluble in 70% (v/v) ethanol. The influence of reducing agents of sodium bisulfite, sodium sulfite and thioglycolic acid on the properties of the glycerol plasticized doughs and the cross-linked bioplastics were investigated. The results showed that reducing agents can be applied to reduce the Young's modulus of the plasticized dough and to improve the Young's modulus of the cross-linked bioplastics. Moisture absorption, weight loss in water, tensile strength, elongation at break and tensile set were studied to characterize the physical properties of the cross-linked bioplastics.

Keywords: Glutenin; Reducing agent; Thermo-molding; Properties

1. Introduction

Wheat gluten has been widely studied due to its cohesive and elastic properties (Payne and Corfield, 1979) as a film former and its good biodegradability, friendly to the environment (Domenek et al., 2004a). The films of wheat gluten or its two main storage proteins, gliadins and glutenins, have been exploited using a solution casting method. Thermal treatment has significant influences on the properties of the films (Ali et al., 1997; Herald et al., 1995; Hernandez-Munoz et al., 2003, 2004a; Kayserilioglu et al., 2003; Roy et al., 1999). Chemical or enzymic treatments have also been applied to modified gluten as film forming materials (Hernandez-Munoz et al., 2003, 2004b; Rayas et al., 1997). Reactive side groups of wheat proteins susceptible to various modifications make it possible to obtain three-dimensional protein networks with appropriate strength and functional properties (Hernandez-Munoz et al., 2005; Marquie, 2001). Dialdehydes and cysteine can be used to cross-link gliadins and glutenins so as to improve water resistance and tensile strength and to lower water vapor permeability of the casting films (Hernandez-Munoz et al., 2004b–d, 2005).

Wheat gluten is able to form a network upon thermo-setting (Sarwin et al., 1993; Strecker et al., 1995) so that it can be processed into films and bioplastics conveniently through thermo-molding (Cuq et al., 2000; Mangavel et al., 2004; Pommet et al., 2005; Sun et al., 2007). In comparison with casting films, thermo-molded films or bioplastics show higher thermal susceptibility and tensile strength while similar microstructure (Jerez et al., 2005; Mangavel et al., 2004). Heating plays an important role in processing of plant protein-based products (Cuq et al., 2000; Domenek et al., 2002; Mo et al., 1999). Glutenins and gliadins are unfolded on heating up to 75 °C, which facilitates the thiol–disulfide interchange and network formation (Schofield et al., 1983).

In a previous paper (Sun et al., 2007), we prepared gluten bioplastic containing glycerol plasticizer by cold-pressing the mixture at room temperature followed by

Abbreviations: ε_B, equibiaxial strain; ε_U, uniaxial strain; H_0, initial sample thickness; R_0, initial sample radii; RH, relative humidity; SDS, sodium dodecyl sulfate; σ_B, equibiaxial stress; σ_U, uniaxial stress; WL, weight loss; WP, water uptake

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thermosetting at high temperatures. In this article, we report the preparation and properties of thermo-molded bioplastics of the glutenin-rich fraction; that is, the gluten residue after extraction of gliadins using 70% (v/v) ethanol. The starch component is not removed so that the proposed method provides a straightforward route for preparing glutenin-rich bioplastics with high strain recovery.

Thiol compounds such as cysteine have been used to mediate the property of gliadin films prepared through solution casting (Hernandez-Munoz et al., 2004c, e) and also gluten bioplastics prepared through thermo-molding (Sun et al., 2007). Chemically reductive thermoforming with sodium sulfite or bisulfite as reducing agent has been applied to keratin and gluten dough formulations to increase the elastic modulus (Pallos et al., 2006; Pavlath et al., 1999). In this article, we mainly focus on the influence of reducing agents of sodium bisulfite, sodium sulfite and thioglycolic acid on flow behavior of a glycerol plasticized glutenin-rich fraction and on the moisture absorption, weight loss (WL) in water and mechanical properties of the thermo-molded bioplastics.

2. Materials and methods

2.1. Materials

Wheat gluten with a protein content $\geqslant$75% and an ash content $\leqslant$0.95% was supplied by Shanghai Wangwei Food Co. Ltd., China. Sodium sulfite, sodium bisulfite, thioglycolic acid and glycerol used were of analytical grade.

The glutenin-rich fraction was obtained from wheat gluten according to the method described by Larre et al. (1997) with slight modification. Gluten (100 g) was dispersed in an aqueous solution (200 ml) of 70% (v/v) ethanol/water mixture at 40 °C for 4 h under continuous stirring. The suspension was centrifuged for 15 min at 4000*g* at room temperature. The supernatant, containing the gliadin-rich fraction, was discarded. The precipitate, consisting mostly of glutenins and starch, was treated again according to the procedure described. The precipitate after the second centrifugation was dried at 40 °C and was ground to pass through a 100 mesh sieve. The protein content in the glutenin-rich fraction was ~58% based on N determination.

2.2. Sample preparation

Sodium sulfite, sodium bisulfite and thioglycolic acid as reducing reagents were dissolved in deionized water to form a 20 wt% solution. Ten grams glutenin-rich fraction, 4 g glycerol and 1 g solution of reducing reagent, corresponding to a composition of glutenin-rich fraction:glycerol: reducing reagent = 100:40:2, was hand-mixed in a mortar to form an apparently homogeneous paste and then mixed on a three-rolling mixer at room temperature.

The paste was molded in a cylindrical mold of polytetrafluorethylene with a size of 20 mm in diameter and 20 mm in height. A strip of polyester film was used to line the inside of the cylindrical mold. The sample surfaces exposed to air were coated with a thin layer of paraffin oil to avoid moisture exchange between the sample and the surroundings. The samples were rested for 3 h at room temperature. The polyester film was then peeled off and the lateral surface of the sample was coated with a thin layer of paraffin oil for the equibiaxial extensional deformation test.

The paste was thermo-molded into bioplastics with a dumbbell shape of 1 mm in thickness and 6 mm in width in a multicavity mold at 125 °C and 10 MPa for 10 min. The length of the work section of the sample was 20 mm. The samples were rested for 48 h before uniaxial extensional deformation testing.

For clarifying the effect of reducing agents, 10 g glutenin-rich fraction and 4 g glycerol were mixed with 1 g deionized water by the same procedure, the sample being denoted as Control.

2.3. Equibiaxial extensional deformation of plasticized glutenin-rich fraction

The cylindrical sample was transferred between two parallel disks coated with a thin layer of paraffin oil as lubricant (Charalambides et al., 2005). An universal testing machine (CMT-4204, Shenzhen SANS Test Machine Co. Ltd., China) was used to compress the sample by moving the lower disk at a constant crosshead speed of 10 mm min^{-1} at 23 °C and 34% relative humidity (RH). The displacement, δ, of the lower disk and the load, F, were recorded simultaneously. Equibiaxial strain ε_B and stress σ_B were calculated according to (Soskey and Winter, 1985; Takahashi et al., 1993)

$$\varepsilon_B = -\frac{1}{2}\ln\left(\frac{H_0-\delta}{H_0}\right) \quad (1)$$

and

$$\sigma_B = \left(\frac{F}{\pi R_0^2}\right)\left(1-\frac{\delta}{H_0}\right), \quad (2)$$

where H_0 and R_0 are the initial thickness and radius of the sample, respectively.

2.4. Uniaxial extensional deformation of thermo-molded bioplastic

The uniaxial extensional deformation test on the thermo-molded dumbbell sample was performed by the universal testing machine with an extension rate of 10 mm min^{-1} at 23 °C at 34% RH. Young's modulus, tensile strength and elongation at break were evaluated from at least five duplicates for each product. Tensile set was measured 48 h after the uniaxial deformation.