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Rheology and processing of gluten based bioplastics

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Abstract

Knowledge of processing effects on the rheological properties of wheat gluten based biomaterials is important for the optimization of the productive process and to obtain biomaterials with suitable mechanical properties. In this paper, the linear viscoelasticity behaviour of glycerol/gluten bioplastics obtained by casting and thermoplastic processing has been studied. The effects of plasticizer content, mixing speed and thermal history were evaluated by oscillatory shear experiments and modulated differential scanning calorimetry in a wide range of temperatures. The mechanical spectrum of these materials was characterized during processing, showing a similar microstructure and, therefore, rheological behaviour at room temperature for both processing procedures. However, bioplastic obtained by mechanical processing showed higher thermal susceptibility, which was related to the denaturation degree and thermosetting and cross-linking potentials of proteins.

Keywords: Wheat gluten; Bioplastics; Rheology; Viscoelasticity; Processing

1. Introduction

During the last 20 years an increasing interest in the use of natural biopolymers has been noticed. The different uses of these new biomaterials go from biodegradable packaging, edible or non-edible, and plastic films to adhesives. Proteins, lipids and polysaccharides have been used as biopolymers to obtain new biomaterials. Proteins derived from plants are a class of renewable materials that are produced at a kiloton scale per annun, e.g. wheat gluten, soy and pea [1,2]. In addition, these new materials present the advantage of biodegradability, wheat gluten biomaterials degradation rates have proved to be among the rates of fast degrading polymers, completely degrading in 50 days when buried in farmland soil [3]. These gluten properties become a great opportunity for adding value to a material, which is often obtained as an agricultural by-product of the food processing industry. Moreover, the importance of new biodegradable materials is not only that they help to reduce waste materials but they could help to preserve petroleum reserves by substituting synthetic polymers [4].

Wheat gluten contains two main groups of proteins, gliadin, also known as prolamin, and glutenin. Gliadin exhibits viscous flow properties without significant elasticity. For cereal technologists, gliadin accounts for the extensionability of wheat flour dough and acts as a filler diluting glutenin interactions. Glutenin is believed to be one of the largest natural molecules. It consists of polymers made from polypeptide chains linked end-to-tail by disulfide bonds [5].

A plasticizer is a major component, required to overcome film brittleness and helping to avoid chipping and cracking of films during subsequent handling and storage. Plasticizers are molecules with low molecular weight, low volatility, which modify the three-dimensional structure of proteins. Wheat gluten films without a plasticizer become brittle and difficult to handle. The plasticizer reduces intermolecular forces and increase polymeric chains mobility. Moreover, the plasticizer reduces the glass transition temperature of the thermoplastic wheat gluten proteins [1,6]. The Tg of wheat gluten has been studied as a function of water, glycerol, and sorbitol contents. These plasticizers had a general behaviour that followed the Couchmann–Karasz relation using a heat capacity (ΔC_p) value of 0.4 J/g K for wheat gluten [7].

Processing films, coatings or other materials based on polymers of agricultural origin requires three main steps:

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breaking of intermolecular bonds (non-covalent and covalent, if necessary) that stabilize polymers in their native forms by using chemical or physical rupturing agents; arranging and orienting mobile polymer chains in desired shape; and, finally, allowing the formation of new intermolecular bonds and interactions to stabilize the three-dimensional network. The shape obtained in the second step is mainly maintained by eliminating the agents used in the first step to break intermolecular bonds. Active sites for bond formation become free and close enough to each other to create new interactions, hydrogen bonds, hydrophobic interactions and disulfide bonds, forming a new three-dimensional network.

Wheat gluten has been proved to be an excellent film-forming agent. Other authors have obtained films by dispersing wheat gluten in an ethanolic solvent containing a plasticizer and acetic acid, then casting the film forming solution and finally drying it [8]. The casting method, or physico-chemical method, of film processing is based on the above-mentioned three steps, using a chemical reactant to disrupt disulfide bonds, dispersing, solubilizing proteins and finally drying it. Previous authors who have studied film formation by the casting method have processed 50 μm thick samples, obtaining good quality films which could be used for food packaging in view of the properties they posses such as opacity, water vapour, oxygen and carbon dioxide permeability, and mechanical properties. However, the use of these films in other applications in which they could substitute synthetic polymers is limited [8–10].

Another way of processing wheat gluten biomaterials is the mechanical method, or thermoplastic processing, which consists of mixing proteins and plasticizer to obtain a dough-like material. Contrary to thermoplastic polymers, gluten viscosity does not decrease upon heating but rather level off or increase due to cross-linking reactions [11,12]. Therefore, the extrusion of proteins is, in general, only possible in a limited window of operating conditions and the material properties of extrudates depend on the processing conditions in a complex way [13–15].

The aim of this work was to compare the linear viscoelastic behaviour of bioplastics prepared by casting method and thermoplastic processing. Thus, the material rheology during its processing has been analysed. Furthermore, viscoelastic behaviour and modulated differential scanning calorimetry (MDSC) have been studied in a wide range of temperature, in order to identify thermal denaturation during processing and to evaluate thermosetting and cross-linking potentials of proteins.

2. Materials and methods

Wheat gluten was provided by RIBA S.A. Protein content was 83 wt.%, lipids 1.5–2 wt.%, and ashes 0.7–0.8 wt.%. Its moisture content was 8 wt.% on dry basis.

Wheat gluten biomaterials were prepared by the casting method according to a slightly modified procedure used by other authors [9,10,16–18]. Wheat gluten was premixed with water and sodium sulphite (3 mg/g wheat gluten) to disrupt S–S bonds. Afterwards, ethanol was added as solvent. Then the plasticizer was added depending on the desired concentration, which were 0.3, 0.4, 0.5, 0.8, 1 g plasticizer/g gluten (G/WG). The pH of the forming solution was adjusted between 4 and 5, according to Gontard's studies on the influence of main process variables on film casting [19].

The solution was then mixed during 30 min at 500 rpm, with an IKA RW-20 Mixer (Germany), in a thermostatic bath at 60 °C, in order to remove air from the solution and to concentrate the solution in wheat gluten proteins by eliminating ethanolic solvent. After the mixing stage, 0.5 g/cm^2 of solution was poured and casted onto a petri disc (9 cm diameter). This method provided a controlled thickness between 1 and 1.2 mm. The material was dried at room temperature. During the drying process the solvent evaporated continuously, increasing protein concentration of the biomaterial and allowing the formation of a new three-dimensional network. The biomaterial thickness was then measured and verified at several positions with a slide gauge before the experiments were carried out.

The mechanical method was carried out in a torque-rheometer, which consists of a batch mixer fitted with two counter-rotating rollers, turning with different angular velocities with a ratio of 3:2 (Rheocord, Haake, Germany). A detailed description of this equipment may be found in the bibliography on rheometry (i.e. Dealy [20]). Torque and product temperature were recorded during the mixing process. The mixing chamber can be considered adiabatic, as it was not cooled. Volume of the chamber (310 cm^3) was filled with approximately 245 g of sample, corresponding to 80% filling ratio. The content of plasticizer was fixed to 0.5 g glycerol/g wheat gluten, and three different mixing speed were tested (15, 50, and 90 rpm).

Oscillatory shear tests, from 0.01 to 100 rad/s, at a constant stress within the linear viscoelastic region, were conducted, at 25 °C, for each sample in a controlled stress rheometer Rheoscope (Haake, Germany), using a serrated parallel plate geometry, 20 mm diameter and 1–3 mm gap. Previously, stress sweep test at 6.28 rad/s were carried out in order to obtain the linear viscoelastic region of the material.

Temperature sweep test, from 25 to 170 °C, were conducted in a controlled rate rheometer ARES (Rheometrics Sci., USA), using a serrated parallel plate geometry, 25 mm diameter and 1–2 mm gap. Measurements were performed at constant frequency (6.28 rad/s) and strain (within the linear viscoelastic region), selecting a 2 °C/min temperature ramp.

MDSC experiments were developed with a Q100 (TA Instruments, USA), using 10–20 mg samples, in aluminiun pans. An oscillation period of 60 s, amplitude of ±0.5 °C, and a heating rate of 5 °C/min, were used. The sample was purged with a nitrogen flow of 50 ml/min.