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Preparation and characterization of cross-linked canola protein isolate films

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ABSTRACT

Cross-linked canola protein isolate (CPI) films were prepared using a bisepoxide as a chain extender by wet cast followed by heat compression. By DSC measurements, it was verified that the cross-linking reaction took place in the CPI matrix and was completed in 10 min at 90 °C. FTIR analysis confirmed that the chain extenders were covalently bonded with CPI chains. The reaction led to the formation of a cross-linked architecture which was revealed by an increase in molecular weight of the modified CPI films. The newly formed chain architecture increased the thermostability of CPI as evaluated by TGA; furthermore, the thermostability increased with the increase in cross-linking degree of the modified CPI films. DMA results of the unmodified CPI film showed that microcosmic phase separation occurred between two major proteins, cruciferin and napin in CPI; however, the extent of phase separation decreased with the increase of chain extenders and finally disappeared because of the increased compatibility between cruciferin and napin. Elastomeric mechanical behavior was observed with the introduction of cross-linked architecture in the modified CPI films. At low humidity of 55%, the cross-linked CPI films showed an increase in tensile strength and a decrease in elongation at break. At high humidity of 98%, the increase in hydrophobicity of cross-linked CPI matrix resisted the decreasing tensile strength seen in unmodified films.

1. Introduction

With a growing interest in green products, the demand for protein-based industrial products is increasing worldwide in the fields of food, gels, adhesives and packaging [1–4]. Canola protein is obtained from the second largest oilseed crop after soy [5,6]; however, the main source of canola protein, canola meal, is not used in human food applications because of the presence of some anti-nutritional compounds, such as glucosinolates, erucic acid, phytates, and phenolics [7,8], making it an ideal candidate for industrial purposes lest its use be relegated to low value animal feed [9]. However, the poor processability, low mechanical properties, and high moisture sensitivity of protein-based biopolymers have limited their applications [10–12]. Accordingly, to increase their mechanical properties and processability, various efforts have been made, such as plasticizing with glycerol [13], propanediol [14–17], polyethylene glycol, or sorbitol [18]; modification of the protein with chemicals [19–21]; or mixing with hydrophobic materials [22–

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25]. The introduction of polar additives can increase mechanical properties of protein-based biopolymer to an extent [26]; on the other hand, this method can also lead to an increase in moisture sensitivity. Blending with hydrophobic materials usually generates immiscible/incompatible phase separation, which deteriorates the mechanical properties of the protein matrix. Chemical cross-linking modification can enhance the formation of covalent bonds in the protein matrix; thus, mechanical properties and barrier properties of the protein-based biopolymer can be further improved.

Many cross-linkers, such as thiol [27], polyurethane and polyisocyanate [28–31], carbodiimide [32], genipin [33], or enzymes [21] can be used to modify the protein matrix. Of these chemicals, aldehydes including dialdehydes and monoaldehydes have been extensively used for cross-linking protein macromolecules, usually by the compression molding method [20,34–39]. Although the use of an aldehyde generally improved the mechanical properties and water-resistance properties of protein-based biopolymers, the optimal aldehyde type and cross-linking density should be experimentally determined. Zárate-Ramírez et al. [40] evaluated the mechanical properties of wheat gluten biopolymers with and without treatment using formaldehyde, glutaraldehyde, and glyoxal by compression molding. It was found that tensile strength of the aldehyde-modified samples was not improved compared to that of aldehyde-free samples. Vaz et al. [41] found that both the tensile modulus and strength of extruded soy protein isolate biopolymer decreased with the addition of glyoxal. They believed that the probability of glyoxal cross-linking via two amine groups of soy located on two adjacent chains was smaller than cross-linking along the same chain during extrusion. Accordingly, the covalent bonds were predominantly introduced within the polypeptide chains instead of between them. In fact, the compression molding method is usually conducted under high pressure and temperature in order to melt and compact the protein matrix [26], which is not easy to apply in industry.

In canola, cruciferin and napin are the two major families of storage proteins, which constitute 60% and 20% of the total protein content in mature seeds, respectively [42]. Cruciferin is a 12S globulin with a high molecular weight (300–310 kDa) and several subunits. Napin is a 2S albumin with a low molecular weight (12.5–14.5 kDa) [43]. Therefore, canola protein is very suitable for the preparation of protein-based films by the casting method because of its water solubility and the well balanced constitution of components with different molecular weight, in which cruciferin can increase mechanical properties of the matrix and napin can act as a plasticizer to increase processability. However, few studies have been conducted on the chemical modification of CPI until now. The objectives of this research are to use canola protein as an ingredient to develop a novel protein-based bioplastic film and to understand the factors that influence the properties of this newly developed product. In this research, 1,4-butanediol diglycidyl ether (BDDE) was used as a chain extender to prepare cross-linked CPI film for the first time. Dermal sheep collagen cross-linked with BDDE was prepared and evaluated after subcutaneous implantation in rats [44]. The results showed cross-linking of dermal sheep collagen with BDDE resulted in biocompatible materials in terms of non-cytotoxicity and non-antigenicity. Additionally, clinical and biocompatibility data spanning more than 15 years support the favorable clinical safety profile of BDDE-crosslinked hyaluronic acid (HA) and its degradation products [45]. Therefore, the usage of BDDE as a chain extender would be anticipated to offer novel properties to CPI in food and industrial applications. Furthermore, the casting method was employed to denature canola protein and unfold the protein chains to an extent in solvent by heating to form a cross-linked protein chain network. The preparation method and the investigation of properties help to increase the knowledge of protein chemical modification and broaden the application fields of canola protein.

2. Materials and methods

2.1. Materials and extraction of CPI from canola meal

Glycerol and 1,4-butanediol diglycidyl ether were purchased from Sigma Aldrich and used as received. The protein extraction procedure was based on the work reported by Manamperi et al. [6] with some minor modifications. Conventional dark-seeded (*Brassica napus*) defatted canola meal was provided by Bunge Canada (Altona, Manitoba). The canola meal was tested for composition which showed 36.5% protein, 11.7% crude fibre, 4.1% crude oil (d.b), 9.8% moisture, and 7.3% ash, in the labs of the Department of Food Science at the University of Manitoba, Canada. The meal was ground into powder using a mill (A10 analytical mill, Ika Works, Wilmington, NC) to pass through a 250 µm sieve and then suspended in distilled water at a ratio of 1/10 (g/ml). The pH of the suspension was adjusted to 12 with NaOH (4 N) with vigorous stirring at 55 °C for 3 h. The first centrifugation took place at 10,000 rpm for 20 min in a Sorvall LYNX 4000 centrifuge (Thermo Scientific, Germany) and the supernatant was collected. The pH of the obtained solution was adjusted to 5 by drop-wise addition of HCl solution (2 N) to allow the canola protein to precipitate. The second centrifugation was conducted and the sediment (protein) was collected and then washed three times with distilled water. The extracted proteins were then dialyzed for 12 h with distilled water with frequent distilled water changes. The protein was recovered after another centrifugation, freeze dried and stored at 5 °C until further use.

2.2. Preparation of cross-linked CPI samples

Cross-linked CPI samples were prepared as follows, using the solvent casting method followed by heat compression. A protein suspension was prepared by mixing 32 g of protein powder with 1200 mL of distilled water. After adding 13.6 g of glycerol, the protein suspension was homogenized via a magnetic stirrer for 30 min. The suspension was heated at 65 °C for 30 min and then cooled down to ambient temperature to obtain a protein solution. The solution was then separated equally into four parts, to three of which 16 mg, 32 mg, and 80 mg of BDDE were added to prepare three cross-linked CPI samples. The solution without added BDDE was used as the control. All of the solutions were stirred for 1 h, and then degassed in a vacuum oven at ambient temperature for

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