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Physicochemical properties and *in vitro* starch digestibility of potato starch/protein blends

Zhan-Hui Lu[a], Elizabeth Donner[a], Rickey Y. Yada[b,c], Qiang Liu[a,*]

[a] Guelph Research and Development Centre, Agriculture and Agri-Food Canada, 93 Stone Road West, Guelph, Ontario, N1G 5C9, Canada
[b] Department of Food Science, Ontario Agricultural College, University of Guelph, Guelph, Ontario, N1G 2W1, Canada
[c] Food, Nutrition and Health Program, Faculty of Land and Food Systems, The University of British Columbia, Vancouver, British Columbia, V6T 1Z4, Canada

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ABSTRACT

This study aimed to investigate effects of starch-protein interactions on physicochemical properties and *in vitro* starch digestibility of composite potato starch/protein blends (0, 5, 10, or 15% protein) during processing (cooking, cooling and reheating). The effect on recrystallization and short-range ordering in starch was studied by light microscopy, differential scanning calorimetry and Fourier transform infrared spectroscopy. The results show that protein in the blend proportionally restricted starch granule swelling during cooking and facilitated amylopectin recrystallization during cold-storage. The facilitating effect of protein diminished with increasing blend ratio. Resistant starch content in the processed blends was positively correlated to intensity ratio of 1053/1035 cm^{-1} in FTIR spectra arising from slow retrogradation of amylopectin ($r^2 > 0.88$, $P \leq 0.05$), whose formation was favored by the presence of protein in the blends and further enhanced by cooling of cooked blends. As a conclusion, starch-protein interaction reduced starch digestibility of the processed blends.

1. Introduction

Potato (*Solanum tuberosum*) ranks third behind rice and wheat in terms of world food production and is the world's number one non-grain food commodity (Camire, Kubow, & Donnelly, 2009). Potatoes provide greater dry matter and protein per unit growing area than cereals. The yields of energy (million calories) and protein (pounds) per acre are 9.2 and 338 for potatoes, 7.4 and 304 for rice, and 3.0 and 216 for wheat, respectively (Ensminger, Ensminger, Konlande, & Robson, 1993). Potato starch has been utilized extensively in food systems because of its unique gel forming properties and the clarity of the gels produced (Yusuph, Tester, Ansell, & Snape, 2003). In its native form, potato starch is classified as resistant starch type II (Englyst, Kingman, & Cummings, 1992), as less than 10% (w/w) of starch is digested within 20 min by alpha-amylase *in vitro* (Oates, 1997). However, after cooking, up to 80% of potato starch will be hydrolyzed within 20 min by enzymes (Lu et al., 2011). This is undesirable to individuals with diabetes or impaired blood glucose control. There would be great nutritional significance if the resistant starch in native potato starch could be retained in the finished food products after processing.

In addition to starch as its major component, potato tubers contain about 2.1% protein (Knorr, Kohler, & Betschart, 1977), accounting for 6–8% protein on a dry weight basis. The quality of potato protein is superior to most major plant proteins (Knorr et al., 1977), with the nutritive value (90–100) approaching that of whole egg protein (100) (Lynch et al., 2012). Compared to proteins from other vegetable and cereal sources, potato protein contains a high proportion of lysine, which is often lacking in such crops (Waglay, Karboune, & Alli, 2014). Unfortunately, the merits of potato protein are not appreciated fully by much of the world compared with wheat gluten protein and soy protein isolates (Ensminger et al., 1993). Potato protein contains approximately 71% patatin/tuberin, 7.6% glutelin, 6.6% albumin, 3% globulin, 1.7% prolamine, and 8.8% other proteins (Kapoor, Desborough, & Li, 1975; Shewry, 2003). Two distinct protein fractions have been commercially produced from raw potato tubers by an isolation process in a minimally processed form involving chromatography and ultrafiltration: a low molecular weight (LM) fraction (4–35 kDa) and a high molecular weight (HM) fraction (> 35 kDa), in a ratio of approximately 50:50 (Lynch et al., 2012). The LM fraction comprises a group of protease

Abbreviations: η^*, Complex dynamic viscosity; DSC, Differential scanning calorimetry; FTIR, Fourier transform infrared spectroscopy; HM, High molecular weight potato protein isolate; LM, Low molecular weight potato protein isolate; DM, Potato dry matter; RDS, Rapidly digestible starch; RS, Resistant starch; SDS, Slowly digestible starch; *G'*, Storage modulus; TPA, Texture profile analysis.

* Corresponding author.
E-mail addresses: zhanhui.lu@agr.gc.ca (Z.-H. Lu), elizabeth.donner@agr.gc.ca (E. Donner), r.yada@ubc.ca (R.Y. Yada), qiang.liu@agr.gc.ca (Q. Liu).

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inhibitor proteins, whereas the HM fraction consists primarily of patatin (Pots, De Jongh, Gruppen, Hamer, & Voragen, 1998).

Large differences in blood glucose levels arising from different starch-containing foods appear to relate to the digestibility of the starch and other factors including the interaction of starch with other food components (Jenkins et al., 1987), together with the nature of the starch itself and its physical form (e.g. raw or cooked, ground or whole) (Thorne, Thompson, & Jenkins, 1983). Proteins have been shown to have an inhibitory effect on starch hydrolysis (Jenkins et al., 1987). Interactions between protein and starch play an important role in texture, mechanical properties, nutrition and digestibility of food products. Protein is found on the surface of starch granules, and it may act as a physical barrier to digestion (Svihus, Uhlen, & Harstad, 2005). Morris (1991) indicated that starch and protein are biological macromolecules and could form different gels (such as complex, filled or mixed gels) involving hydrogen bonding, electrostatic forces, van der Waals forces and entanglement. Jenkins et al. (1987) highlighted the advantages of natural starch-protein interactions in wheat-based foods for patients with diabetes. Jamilah et al. (2009) stated that the interaction between protein and starch is mainly electrostatic in nature, between the anionic groups of the starch and the positively charged groups of the protein. Zeng et al. (2010) confirmed by Fourier transform infrared spectroscopy (FTIR) that intermolecular interaction between corn starch and hydrophilic protein occurred. Hydrogen bonding is the most important intermolecular interaction determining the properties of a starch matrix; these bonds can be present as either bound hydroxyls or free hydroxyls in solid carbohydrates, distributed above 3000 cm^{-1} of the infrared (IR) absorbance bands. If free hydroxyls become bound hydroxyls, the IR absorbance band in the hydroxyl region above 3000 cm^{-1} shifts to lower frequency (Liang & Ludescher, 2015). However, there is a lack of information on potato starch-protein interaction, and its effect on starch digestibility of potato-based foods.

The objectives of this study were to investigate the effect of starch-protein interactions in a model system made from isolated potato starch and potato protein, on the thermal properties (gelatinization, denaturation and retrogradation), gel rheological properties (at small and large deformation), short-range ordering in starch molecules during processing (cooking, cooling and reheating), and starch digestibility *in vitro* in raw, cooked, cool-stored and reheated gels. Two types of potato protein isolates (low and high molecular weight) were used up to a level similar to that found in potato dry matter. Potato dry matter was included as a reference in order to compare the effect from naturally occurring starch-protein interactions with any potential starch-protein interactions in the model system. The results are expected to be informative for manipulation of potato-based foods with different digestibility and for full utilization of potato protein resources.

2. Materials and methods

Potato dry matter and isolated starch (*var.* CV92056-4) were as per our previous study (Lu et al., 2011). Their total starch content, apparent amylose content and protein content were 69.6% and 98.2%, 25.7% and 31.4%, and 12.6% and 0.7%, determined by AACC International (1999) method 76-13, iodine colorimetry and Dumas method (NA 2100 Protein, Thermo-Quest Italia S.P.A., Ann Arbor, MI, USA), respectively. Two potato protein isolates (low molecular weight protein isolate, LM; and high molecular weight protein isolate, HM) were supplied by AVEBE (Veendam, The Netherlands). According to the manufacturer, LM has a protein concentration of >95%, a molecular weight between 4–35 kDa, and isoelectric point of >6. HM has a protein concentration of 92%, a molecular weight of >35 kDa, and isoelectric point of <6. All materials were stored at −20 °C before use.

2.1. Sample preparation

2.1.1. Native blend samples

Potato protein isolate (LM) was individually blended with potato starch at ratios of 0, 5, 10, and 15% (w/w) in zippered plastic bags (100 g in total), by step-wise addition of small amounts of potato starch to the protein sample while whisking thoroughly for 5 min until a homogeneous mixture was obtained. The uniformity and correct proportion of blend samples was verified by sampling from the top, bottom and centre of the bag for protein content analysis. The composite blends were labelled as LM0 (pure starch), LM5, LM10, LM15 and LM100 (pure protein isolate). HM was prepared at the 15% level (HM15). The experimental design was more focused on LM because of its high isoelectric point; the LM could be positively charged to interact with starch molecules by electrostatic complexing in our blend system. Potato dry matter (DM) was used directly as a reference.

2.1.2. Processed samples (cooked, cooled and reheated)

The processed samples were prepared by cooking, cooling and/or reheating a 30% (w/w) suspension (in water) of the above prepared blends or DM powder. The suspension (30 g) was sealed in a 50 mL centrifuge tube and hydrated at room temperature for 2 h followed by cooking in a boiling water bath for 10 min, with vortexing at 2 min intervals to prevent solid precipitation. The cooked paste was immediately frozen at −80 °C. Cooled sample was obtained by storing the freshly cooked sample at 4 °C for 24 h and then freezing at −80 °C. The reheated sample was obtained by reheating the cooled sample in a microwave oven at 1.1 kW for 2 min, and then freezing at −80 °C. Frozen samples were freeze dried and ground by a pestle and mortar to pass through a 500 μm sieve.

2.2. Thermal properties

Thermal analyses for starch gelatinization/retrogradation and protein denaturation in starch/protein blends and dry matter were performed using a differential scanning calorimeter (2920 Modulated DSC; TA Instruments, New Castle, DE, USA) equipped with a refrigerated cooling system. Briefly, the uncooked powder (12 mg) was weighed into high-volume pans and distilled water was added to make suspensions with 70% moisture content. The pan was sealed hermetically and equilibrated overnight at room temperature, and then scanned from 5 to 180 °C at a heating rate of 10 °C/min. After cooling to room temperature, the sample pans were stored at 4 °C for 14 days to allow starch to retrograde, and then reheated at 10 °C/min from 5 to 180 °C. The instrument was calibrated using indium and an empty pan as a reference. Before and after scanning, the sealed pan was weighed to confirm that no leakage had occurred. The onset temperature (T_0), peak temperature (T_p), conclusion temperature (T_c) and transition enthalpy (ΔH) of each curve were determined using TA Universal Analysis software. Gelatinization enthalpy was normalized by subtracting protein denaturation enthalpy from the total enthalpy in the corresponding thermograms.

2.3. Rheological measurements

2.3.1. Small deformation test

Dynamic viscoelasticity of the samples was measured in dynamic shear mode using a strain-controlled rheometer (ARES, TA Instruments, New Castle, DE, USA), operated with a parallel-plate geometry with a 25 mm diameter, as described in previous work