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Effect of porcine plasma protein hydrolysates on long-term retrogradation of corn starch

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ABSTRACT

The potential effect of porcine plasma protein hydrolysates (PPPH) on the long-term retrogradation of corn starch (CS) was investigated. The differential scanning calorimetry results showed that PPPH significantly reduced the retrogradation enthalpies (ΔHr) of CS ($P < 0.05$), obviously decreased the crystallization rate constant (k), and enhanced the Avrami exponent (n) ($P < 0.05$). Low-field nuclear magnetic resonance analysis demonstrated that the spin–spin relaxation time (T_2) remarkably increased with increasing PPPH concentration during storage at 4 °C for 28 days ($P < 0.05$). The X-ray diffraction results revealed that the relative crystallinity of retrograded CS decreased from 13.04% to 8.73% with the addition of PPPH. Fourier transform infrared spectroscopy analysis demonstrated that the addition of PPPH led to a decrease in hydrogen bonds within starch. The results demonstrated that the addition of PPPH apparently played a crucial role in retarding the long-term retrogradation of CS.

1. Introduction

Starch is one of the most common polysaccharides and is widely used to improve the quality of food products as a thickener, gelling agent, colloidal stabilizer, water retention agent, and adhesive (Tian, Li, et al., 2009). However, retrogradation is an unavoidable property of starch, which leads to quality deterioration of starchy products during storage. It is known that amylose and amylopectin have different roles in starch retrogradation. Aggregation of amylose is mainly due to short-term retrogradation, which occurs at the beginning of storage (Chen, Ren, Zhang, Tong, & Rashed, 2015). Nevertheless, long-term retrogradation of starch is a more important problem caused by the crystallization of amylopectin, (Gudmundsson, 1994), which usually occurs in starch-based products subjected to longer storage. Additionally, long-term retrogradation destroys the texture, quality, digestibility and functionality of starch-based products (Mutungi, Passauer, Onyango, Jaros, & Rohm, 2012). Many methods have been suggested to inhibit or decrease the long-term retrogradation of starch, such as chemical modification (Adebowale & Lawal, 2003), physical modification (Liu & Thompson, 1998), enzymatic treatment (Li et al., 2016), and addition of some non-starchy substances (e.g., food hydrocolloids, polysaccharides, salts, fatty acids, amino acids, and plant derivatives) (Chen, Zhou, Yang, & Cui, 2015; Peterson, Eller, Fanta, Felker, & Shogren, 2007; Wang et al., 2017; Xu et al., 2013; Zhang, Sun, Zhang, Zhu, & Tian, 2015; Zhou, Robards, Helliwell, & Blanchard, 2007).

Protein hydrolysates prepared with different types of enzymes are increasingly applied as nutritional additives in the food industry and also provide many health benefits, which have mainly been attributed to the bioactive peptides that they contain. When protein hydrolysates are incorporated into food products, their components may interact with other ingredients, such as starch. In a previous study, we found that porcine plasma protein hydrolysates (PPPH), which were hydrolysed via Alcalase for 5-h, possessed the strongest antioxidant activity, such as reducing power, free radical scavenging activities, metal chelating capacities and inhibition of lipid oxidation (Liu, Kong, Jiang, Cui, & Liu, 2009). Meanwhile, 5-h Alcalase hydrolysis obviously increased the protein solubility and remarkably decreased the surface hydrophobicity, emulsifying capacity and foaming capacity of the plasma protein (Liu, Kong, Xiong, & Xia, 2010). Our study also indicated that 5-h Alcalase hydrolysed plasma protein was composed of a large amount of charge-carrying amino acids, such as glutamic acid, leucine, aspartic acid, lysine, valine and cysteine (Liu, Kong, Li, Liu, & Xia, 2011). We also demonstrated that PPPH had a stronger regulatory effect on the pasting properties of corn starch (Kong, Niu, Sun, Han, & Liu, 2016). Furthermore, Goel, Singhal, and Kulkarni (1999) postu-

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lated that casein hydrolysate may readily interact with amylose and outer branches of amylopectin, affecting the paste viscosity and gelatinization temperature of corn starch. Cui, Fang, Zhou, and Yang (2014) suggested that the addition of charge-carrying amino acids (such as lysine, glutamic acid, arginine, and aspartic acid) could significantly modify the physicochemical properties and improve the nutritional values of potato starch. Meanwhile, Liang and King (2003) claimed that some special amino acids or peptides could obviously influence the gelatinization behaviour of rice starch. It is thought that the alkyl side chains of hydrolysates may be trapped in the helical structure of starch, resulting in the formation of complexes that have a wide assortment of molecules (Godshall & Solms, 1992). Lian, Zhu, Wen, Li, and Zhao (2013) concluded that some polypeptides from soybean protein hydrolysates might interact with maize starch and influence the physicochemical properties of starch during food processing. More importantly, Ribotta, Colombo, and Rosell (2012) confirmed that starch modified by protein hydrolysates increased the enthalpy of starch gelatinization through electrostatic repulsion and promoted synergistic interactions between hydrolysates and starch during gelling.

Despite the fact that some observations on the gelatinization properties of starch-hydrolysates or starch-amino acid mixtures have been reported, there are few studies on the impact of protein hydrolysates on the long-term retrogradation of starch. The objective of the present study was to investigate the inhibition of PPPH on the long-term retrogradation of gelatinized corn starch (CS). Moreover, a possible impacting mechanism was proposed with the aid of differential scanning calorimetry (DSC), X-ray diffraction (XRD), low field nuclear magnetic resonance (LF-NMR) and Fourier transform infrared spectroscopy (FTIR).

2. Materials and methods

2.1. Materials

Porcine plasma protein, which contains 85% protein (based on the total weight basis) was purchased from Beidahuang Meat Corporation (Harbin, Heilongjiang, China). Commercial corn starch was obtained from ChangChun DaCheng Corn Products Co. (Changchun, China) and used after drying in an oven at 80 °C for 24 h. All chemicals and reagents were of analytical grade.

2.2. Preparation of PPPH

PPPH was prepared according to the method described by Liu et al. (2010). Briefly, a suspension of porcine plasma protein (40 mg protein/mL) was preheated at 95 °C for 5 min. The suspensions were then hydrolysed using Alcalase at 55 °C for 5 h. The ratio (E/S) of enzyme to substrate was 2:100 (g/g). Meanwhile, the suspensions were adjusted to pH 8.0 with 1 M NaOH during hydrolysis. After hydrolysis, the suspensions were neutralized with 1 M HCl to pH 7.0. Then, the suspensions were heated at 95 °C for 5 min to inactivate the enzyme. The degree of hydrolysis (DH) of PPPH was 17.6%. The PPPH samples were desalted and lyophilized. The freeze-dried hydrolysates were sealed in polyethylene bags and then stored at 4 °C. The proximate composition (based on the total weight basis) of lyophilized PPPH was as follows: 84.6% of protein, 10.1% of moisture, 1.5% of fat and 3.7% of ash.

2.3. Preparation of retrograded starch samples

Gelatinized starch samples were prepared according to the method of Chen, Ren, et al., (2015) with some modifications using rapid viscosity analyser (RVA) (RVA-4, Newport Scientific, Warriewood, Australia). Native CS (3.5 g, dry basis) was suspended in aluminium RVA sample canisters with 25 mL of distilled water, and 0, 2, 4, 6, and 8% (w/w) PPPH at dry starch weight basis was then added to the starch slurry. A programmed heating and cooling cycle was used in which the samples were held at 50 °C for 1 min, heated to 95 °C at 12.2 °C/min and held for 2.5 min at 95 °C. The samples were then cooled to 50 °C (cooling rate of 11.8 °C/min) and maintained for 2 min. Following gelatinization, all of the samples were stored at 4 °C to perform the retrogradation process. The stored samples were taken out at set time intervals and used for LF-NMR, XRD, FTIR, and DR analyses.

2.4. Differential scanning calorimetry measurements

The retrogradation properties of CS with different concentrations of PPPH during storage at 4 °C were analysed using a Model Q20 DSC machine (TA Instruments, Inc., New Castle, DE, USA) under an ultrahigh-purity nitrogen environment. The equipment was calibrated with indium and an empty aluminium pan. Different concentrations of PPPH solutions were pre-created using distilled water. Then, 6 μL of each PPPH solution was placed in an aluminium pan which already contained 3 mg of native CS (dry basis), to make final concentrations of 0, 2, 4, 6, and 8% PPPH to CS (at dry starch basis, w/w). All of the pans were hermetically sealed at room temperature for 12 h to fully hydrate the samples. A thermal scan was conducted from 30 to 110 °C at a constant heating rate of 10 °C /min to perform the gelatinization process. The transition temperatures (T_o, T_p, and T_c) and total transition enthalpy changes (ΔHg) were recorded. Following gelatinization, all of the above aluminium pans were stored at 4 °C for 1, 3, 5, 7, 14, 21, and 28 days to perform the retrogradation process. Then, the retrograded starches were rescanned from 30 to 100 °C at a constant rate of 10 °C /min to melt the retrograded amylopectin crystallites. The transition temperatures (T_o and T_c) and melting enthalpy (ΔHr) were recorded again.

The Avrami equation (Beck, Jekle, & Becker, 2011) was applied to evaluate the kinetics of starch retrogradation (especially amylopectin). The model is described as follows:

$$X(t) = \frac{\Delta H_t - \Delta H_0}{\Delta H_\infty - \Delta H_0} = \exp(-kt^n)$$

where X(t) is the volume fraction of crystallized amylopectin at time t and ΔH_0 and ΔH_t are the enthalpy changes developed at time 0 and time t, respectively (where ΔH_0 was zero in this study). ΔH_∞ is the limiting enthalpy change (28 d for all samples). k is the rate constant, and n is the Avrami exponent, which were obtained from a linear regression of the retrogradation enthalpy data:

$$\ln\left[-\ln\left(1-\frac{\Delta H_t}{\Delta H_\infty}\right)\right] = n\ln t + \ln k$$

2.5. Spin-spin relaxation (T_2) measurements

The transverse relaxation time (T_2) was measured using a Bruker benchtop LF-NMR analyser (mq-20, Bruker Corporation, Germany) with a magnetic field strength of 0.47 T and a resonance frequency of 20 MHz for protons. The gelatinized samples prepared as described in Section 2.3 were transferred to cylindrical glass NMR-tubes (18 mm in diameter) and sealed with parafilm, and the tubes were stored at 4 °C for 1, 3, 5, 7, 14, 21, and 28 days. At the conclusion of the storage time, the retrograded starches were equilibrated at room temperature (25 °C) for 1 h before measurement. Then, the T_2 of each sample was directly measured by LF-NMR using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence (Carr & Purcell, 1954; Meiboom & Gill, 1958), with an interpulse