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Diverse rheological properties, mechanical characteristics and microstructures of corn fiber gum/soy protein isolate hydrogels prepared by laccase and heat treatment☆

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ABSTRACT

Two types of corn fiber gums (CFGs) were extracted from corn fibers (CFs) obtained from wet or dry corn milling processing. Both CFGs could form hydrogels induced via laccase, but CFGs isolated from wet milling CFs exhibited higher storage modulus (G′) and better mechanical strength as obtained from rheological testings. Afterwards, CFGs from wet milling CFs and soy protein isolate (SPI) were used to fabricate CFG-SPI double network (DN) hydrogel using laccase and heat treatment processes, in which CFG solution formed the first gel network through laccase oxidation, while SPI formed the second network through heating. When compared with single network (SN) CFG-SPI hydrogel, the DN CFG-SPI hydrogel looked more firm and complete with better elasticity. The rheological testings showed that both the storage modulus (G′) and loss modulus (G″) of DN hydrogel were higher than SN hydrogels of CFGs or SPI. Moreover, the CFG-SPI DN hydrogels exhibited more applicable hardness compared to SPI hydrogels and better deformation ability compared to CFG hydrogels. The results from scanning electron microscopy indicated that these CFG-SPI DN hydrogels had more regular, denser inner structure and smoother surface than SN hydrogels.

1. Introduction

Hydrogel is a kind of polymeric materials with a three-dimensional structure maintained by covalent or non-covalent interactions between macromolecules (Kopeček, 2007). The hydrogels work was first proposed by Wichterle & Lim (1960), and now these are widely used in food processing, drug delivery, tissue engineering and biosensors. For instance, hydrogels were the first biomaterials rationally designed for human use (Kopeček & Yang, 2007). There are three commonly used methods for hydrogel biomaterials synthesis: (a) chemical crosslinking and copolymerization, (b) chemical crosslinking of reactive polymer precursors, and (c) chemical crosslinking via polymer-polymer reaction. The hydrogels synthesized by these methods have poor mechanical properties and their detailed structures are not well characterized due to formation of many side products containing cycles, unreacted pendant groups and entanglements (Kopeček, 2007).

The polysaccharide and protein are two important raw materials in food hydrogel, and scientists always use them to design food structure in order to obtain the desired properties.

Polysaccharides such as starch, cellulose, glucan, chitosan and arabinoxylan (AX) are usually used to form hydrogels. Arabinoxylans are hemicelluloses mainly found in cereal grains, and they are among the major cell-wall polysaccharides of wheat and corn endosperm (Izydorczyk & Dexter, 2008; Qiu et al., 2016). Arabinoxylan consists of a linear backbone of β-(1 → 4)-linked D-xylopyranosyl units to which α-L arabinofuranosyl substituents are attached through O-2 and/orO-3 (Izydorczyk & Biliaderis, 1995;

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Martínez-López et al., 2013). Corn fiber gum (CFG) is an arabinoxylan (hemicellulose B) isolated from deoiled and destarched corn fiber by analkaline hydrogen peroxide extraction process (Qiu et al., 2015; Yadav, Fishman, Chau, Johnston, & Hicks, 2007). Different corn fibers (raw materials) and extraction methods lead to different yield of CFG and other components (Yadav, Johnston, Hotchkiss, & Hicks, 2007). Previous studies on CFG were mainly focused on its composition (Ayala-Soto, Serna-Saldívar, García-Lara, & Pérez-Carrillo, 2014a), extraction and emulsifying properties (Liu et al., 2015; Yadav, Moreau, & Hicks, 2007). CFG contains a hydrophobic protein, which contributes towards its very good emulsifying properties (Yadav, Moreau, Hotchkiss, & Hicks, 2012; Yadav, Nunez, & Hicks, 2011). In addition to protein, CFG contains a small amount of ferulic acid (FA) covalently linked via an ester linkage to some of the arabinose residues (Smith & Hartley, 1983). One of the most important properties of AX is its ability to form gels by covalent cross-linking through its ferulic acids (FA) oxidation by chemicals (ferric chloride, ammonium persulphate) or enzymatic (laccase/O_2, peroxidase/H_2O_2) or free radical-generating agents (Carvajal-Millan et al., 2007; Martínez-López et al., 2011; Schooneveld-bergmans, Dignum, Grabber, Beldman, & Voragen, 1999; Vansteenkiste, Babot, Rouau, & Micard, 2004). Arabinoxylan molecules form gels by covalent cross-linking of AX chains through dimerization and terpolymerization of ferulic acid substituents under the action of laccase (Figueroa-Espinoza & Rouau, 1998; Geissman, Neukom, 1973; Hoseney & Faubion, 1981; Izydorczyk, Biliaderis, & Bushuk, 1990). Five main dimers of ferulic acid (di-FA) (5-5′, 8-5′ benzo, 8-*O*-4′, 8-5′, and 8-8′ forms) and the presence of a trimer of ferulic acid (tri-FA) (4-*O*-8′, 5′-5″-dehydrotriferulic acid) have been identified in gelled AX (Carvajal-Millan, Guigliarelli, Belle, Rouau, & Micard, 2005; Carvajal-Millan, Landillon et al., 2005; Figueroa-Espinoza, Morel, & Rouau, 1998; Schooneveld-bergmans, Dignum, Grabber, Beldman, & Voragen, 1999; Vansteenkiste et al., 2004). Previous studies have indicated that the gel strength of water-extractable AX extracted from endosperm of wheat kernel was associated with the amount of its FA while the crosslinking was induced by laccase (Carvajal-Millan, Landillon et al., 2005; Carvajal-Millan, Guilbert, Morel, & Micard, 2005). It was also found that AXs extracted from corn bran by mild alkali treatment formed strong gels through FA crosslinking by the action of laccase (Kale, Hamaker, & Campanella, 2013). Although there are a lot of researches have been down on enzymatic cross-linking of FA containing polysaccharides, a very few studies have been conducted to examine the gelling ability of CFG through laccase inducement.

Besides polysaccharide, protein is another common gelling agent used in food industry, and protein gelation or gelation between polysaccharide and protein are prepared. Polysaccharide-protein double network (DN) hydrogel was first prepared by Gong, Katsuyama, Kurokawa, and Osada (2003), who reported that such DN hydrogel was able to overcome the disadvantages of single polysaccharide or protein hydrogels. Some other investigators found that when whey protein isolate gels was combined with konjac glucomannan or xanthan gum had higher gel strength and less gelation time (Bertrand & Turgeon, 2007; Tobin, Fitzsimons, Chaurin, Kelly, & Fenelon, 2012). Some more study indicated that carrageenan can change the denaturation and gelling rates of soybean protein through its synergistic effect at a pH value lower than protein isoelectric point (Zhou, 2005). However, the gelation process and the performance of CFG and protein DN hydrogels have not been studied.

In the current study, two different types of corn fiber gums, (a) wet-milling CFG (W-CFG) and (b) dry-milling CFG (D-CFG), were extracted from corn fibers collected from wetand drycorn milling facilities, respectively, and a DN hydrogel using W-CFG and soy protein isolate (SPI) were fabricated by heating them in presence of laccase. Then the rheological properties, mechanical properties and microstructure of CFG hydrogel, SPI hydrogel, CFG/SPI single network hydrogel and CFG-SPI DN hydrogel were studied and compared.

2. Materials and methods

2.1. Materials

Wet and dry milled corn fiber samples were obtained from the local corn kernel processors. Soy protein isolate (SPI) was kindly provided by Fuji oil Co.Ltd Beijing Branch. Laccase from Trametesversicolor (E.C.1.10.3.2) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Heat-resistant α-amylase was purchased from Aladdin Industrial Corporation (Shanghai, China). All other reagents were of analytical grade.

2.2. Isolation of CFG

Corn fiber (CF) was ground to 40-mesh, and de-oiled by agitating it in hexane (CF to hexane weight ratio 1:7) on a rotatory shaker (100 rpm) for 2 h. Starch was removed from the 20-mesh de-oiled fiber by treating with Termamyl α-amylase (Doner, Chau, Fishman, & Hicks., 1998). CFG was extracted from the de-oiled and de-starched fiber using a modified alkaline hydrogen method (Yadav, Johnston et al., 2007). In brief, the de-oiled and de-starched corn fiber (100 g) was suspended in 0.25N sodium hydroxide solution (500 ml) and stirred using a mechanical stirrer at 100 rpm at 25 °C in dark for 4 h. The reaction mixture was centrifuged at 7400 × g for 15min. The supernatant was separated from the residue by decantation. The pH of the supernatant was adjusted to 4.0–4.5 by adding concentrated HCl to precipitate hemi-cellulose A (acid-insoluble arabinoxylan, “Hemi. A”). and centrifuged at 7400 × g for 15min to separate the precipitate. The supernatant was collected and precipitated with 4 vol of 100% ethyl alcohol and stored at 4 °C for 4 h for complete precipitation. The precipitate was lyophilized to get dry product.

2.3. Analysis on ferulic acid and protein

A weighed quantity of standard FA was dissolved in 2 mL, 50 mmol/L PBS buffer solution (pH = 7.0) to obtain 20 μg/ml FA solution, which was diluted to get FA concentrations in the range of 2–11 μg/ml. The absorbance of FA at different concentrations was measured at 290 nm against a reagent blank solution containing the same PBS buffer solution by a UV visible spectrophotometer (T9, PuXi Company, China).

The protein content of CFGs was determined by Coomassie Brilliant Blue staining analysis (Bradford, 1976).

2.4. Hydrogels preparation

CFG (isolated from wet milling corn fiber) solution (2%, w/v) was prepared by dissolving it in deionized water and stirring at room temperature for 6 h. SPI solution, (13%, w/v) was prepared in deionized water by stirring for 4 h and stored at 4 °C overnight to promote a complete hydration of the protein molecules.

Then to make the solution of CFG and SPI mixture, CFG was added slowly to the fully hydrated SPI solution (hydrated as given above) and stirred at room temperature until fully dissolved. The solution of CFG-SPI mixture was cultured at 25 °C for 2 h after adding laccase (1.670 nkat/mg CFG) to generate the first gel network of CFG. Subsequently, the mixture was incubated on a water bath (80 °C) for 30min and quickly cooled down to room temperature by running tape water for the formation of second gel

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