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Rheological properties of soy protein isolate solution for fibers and films

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ABSTRACT

For the first time, rheological behavior of soy protein isolate (SPI) solution with high concentration for fibers and films was studied. The results showed that SPI could be readily dissolved in urea/sodium sulfite aqueous system, and the SPI solution is suitable for wet spinning and film casting. The effects of concentration, temperature, and shear rates on the rheological properties of SPI solution were studied. Viscosity of SPI solution decreases with increasing temperature, which is good for the preparation of solution with high concentration and regenerated SPI fibers/films with good properties. All solution samples exhibited thixotropic behavior, which were different from traditional polymer solution for wet spinning and film casting process. Both in forward and backward measurements were carried out by the Power Law model. Under constant shear rates (80-160 s^{-1}), 18 wt% SPI solution was chosen to study the dependence of viscosity on time. Second order structural kinetic model, Weltman model, first-order stress decay models with zero and none-zero equilibrium stress values were used to fit the rheological data. Among the four models, Weltman model is more appropriate to fit the thixotropic data.

1. Introduction

Regenerated protein fibers are prepared via purification, dissolution, and spinning processes from animal proteins or plant proteins (Xu, Liu, Mi, Xu, & Yang, 2015). Different from synthetic polymer fibers, regenerated protein fibers possess good biocompatibility, biodegradability, good hygroscopicity and soft hand, and thus are sustainable and environmentally friendly material (Poole, Church, & Huson, 2009). Study on the regenerated protein fibers began from 1930 to 50s, such as casein milk fibers, peanut fibers, zein fibers, and soy protein fibers (Hearle, 2007). Among all the plant protein resource, soy has the most protein amount (37–42%) and big production (282 million tons in 2014).

Pure soy protein fibers were studied from 1940. And the first patent about soy protein fibers was authorized to Toshiji Kajita and Ryohei Inoue (Inoue & Kajita, 1940). In 1945, Boyer from Ford Motor Company also applied a patent (William, Robert, & Crupi, 1945). However, the production of mid-twentieth soybean protein fibers was ceased at the end of the World War II (Rijavec & Zupin, 2011). Huang, Hammond, Reitmeier, & Myers, 1995 prepared regenerated soy protein fibers again via wet spinning in 1995 (Huang et al., 1995). Since 2000, researchers began to study composite soy protein fibers (Li, Zeng, Wang, Yang, & Wang. 2008; Zhang, Li, & Yu, 2011). However, the content of soy protein is less than 30% in the composite fibers.

Soy protein can also be prepared to edible film or coatings. These biopolymer films have great potential application in the field of edible packaging. They act as barriers to control transferring of gas and volatile flavors (Gennadios, Brandenburg, Weller, & Testin, 1993; Park, Rhee, Bae, & Hettiarachchy, 2001). There are two main approaches to make packing materials from proteins: wet processing and dry processing. The type of bonds stabilizing the protein film matrix is mainly hydrophobic, electrostatic, hydrogen and/or covalent, the relative importance of them being mainly dependent on the biochemical properties of each protein and the production method/processing conditions (Gómez-Estaca, Catalá, &Hernández-Muñoz, 2016). Researches usually differentiate two kinds of dry processing: thermo-pressing and extrusion. SPI films can be prepared by the use of extrusion (Chan, Lim, Barbut, & Marcone, 2014) and thermo-pressing (Garrido, Etxabide, Peñalba,

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de la Caba, & Guerrero, 2013) independently, sometimes they are combined, using extrusion for the mixing and partial modification of the components, and then obtaining the materials by thermo-pressing (Gómez-Estaca, Catalá, &Hernández-Muñoz, 2016).

To prepare fibers or films with good properties, the key step is dissolution of soy protein. Due to disulfide bond, hydrogen bond, hydrophobic effect and other secondary bond, soy protein is globular (Zhao, Zhao, Xu, & Yang, 2015). During the dissolving process, globular conformation should be modified to form molecules coil-denaturation. Denaturation is beneficial to modify the entanglement among proteins, leading to improvement of fiber strength after drawing. Hydrogen bond and disulfide bond were usually dissociated for dissolving. Urea was found to be an effective swollen agent for soy protein, because O and H atom in urea molecule can react with −OH in soy protein to break hydrogen bond (Kinsella, 1979). Disulfide bonds can be ruptured by oxidation, reduction, and exchanging effect (Wall, 1971). Among the above approaches, reduction is preferred. Most common reductants include sodium cyanide (Krull & Friedman, 1967), sodium sulfite (Reddy & Yang, 2007), cysteine (Xu & Yang, 2014; Xu, Cai, Xu, & Yang, 2014) and so on.

To date, wet spinning and electrospinning are two main methods to fabricate protein fibers. Steady spinning solution is the precondition no matter whichever method above will be used. Rheological properties of spinning solution play an important role in spinning process, structural formation, and fibers' properties, respectively, and thus are usually studied as an important parameter for wet spinning. Puppo et al. studied the effect of pH, concentration, and ionic strength on the rheological properties (Puppo & Añón, 1999). Varzakas et al. studied the gel strength from soy protein isolate and soy protein concentration (Varzakas, Labropoulos, & Anestis, 2011). Kim et al. studied the effect of volume fraction of oil droplet on the rheological properties (Kim, Renkema, & van Vliet, 2001). Murekatete et al. studied the gelation and rheological properties induced by salts and acid (Murekatete, Hua, Chamba, Djakpo, & Zhang, 2014). Wagner et al. studied the influence of concentration, water-imbibing capacity (WIC), salt addition, and thermal treatment on viscosity and rheological behavior of commercial soy isolates (Wagner, Sorgentini, & Anon, 1992). They also found that the apparent viscosity of dispersions of SPI depends on the WIC, the morphology and size of the particles, and the interaction of the hydrated particles (Añón, Sorgentini, & Wagner, 2001). However, these researches were always carried out for the applications of soy protein as food ingredients. In addition, viscosity also plays an important role in film casting. Until now, rheological study on the high concentration SPI solution for fibers and films has not been reported yet.

In this study, soy protein aqueous solutions for wet spinning and film casting were prepared with urea as swollen agents and sodium sulfite as reductants. Effects of concentration, temperature, and shear rates on rheological properties were studied by rotational rheometer. Soy protein solution with 18 wt% concentration was chosen to study the thixotropic behavior by fitting the data with four theoretical models.

2. Experimental

2.1. Materials

Soy protein isolate (SPI, partially denatured) was a gift from Archer Daniels Midlands Company. It contains moisture (<6%), protein (>90%), fat (<4%), and ash (<5%). Urea, sodium sulfite, and paraffin oil were purchased from VWR International, Bristol. All reagents were analytical grade and used as received.

2.2. Preparation of SPI solutions

In a typical experiment, SPI powder (100 g) was mixed with 8 M urea solution (399 g) with 1% (w/w) sodium sulfite on weight of SPI used. The mixtures were swelling for 24 h and then stirred at 80 °C for 2 h to ensure the complete dissolution. The resultant solutions (20 wt%) came out tan and then were centrifuged to degas them at 9792×*g* for 10 min at ambient temperature (Allegra 25R Centrifuge, Beckman Coulter). The SPI solution was hermetically stored at ambient temperature and protected against moisture evaporation. Under the same conditions, SPI solutions with other concentrations (16 wt%, 18 wt%, and 22 wt %) were also prepared. During fiber extrusion/film casting, unreacted sodium sulfite will be washed away at high liquor-to-fiber/film ratio and subsequent 2 to 3 cycles of washing. Therefore, re-formation of disulfide bonds during solidification of fiber/film will not be avoided or reduced by extra sodium sulfite in the spinning dopes.

2.3. Rheological measurement

Rheological analysis was carried out on a rotational rheometer, R/S plus (Brookfield, U.S.A.). A coaxial spindle/chamber geometry (CC 25) was used. Shear viscosity $\eta\,(\dot{\gamma})$ was measured as a function of shear rate $\dot{\gamma}$ in the range of 0–240 s^{-1}. For each measurement, a fresh SPI solution was prepared, and then degassed SPI solution was poured into the geometry instrument, which had been kept at each measurement temperature without pre-shearing or oscillating. To prevent dehydration during rheological measurements, a thin layer of low-viscosity paraffin oil was spread on the exposed surface of the measured solution. For the 22 wt% sample, high viscosity cannot be detected by this rheometer due to out of upper limit at the temperatures lower than 40 °C. So 16 wt%, 18 wt%, and 20 wt% samples were chosen to study the influence of concentrations on the rheological behavior.

Flow behavior was described by the fitting of experimental data with the Power Law model:

$$\sigma = k\dot{\gamma}^n \quad (1)$$

Where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), k is the consistency coefficient (Pa s^n) and n is the flow behavior index.

The area of hysteresis loop was obtained by the difference between integrating the area for forward and backward measurements from $\dot{\gamma}_1$ (initial shear rate) to $\dot{\gamma}_2$ (final shear rate):

$$\text{Hysteresis loop area} = \int_{\dot{\gamma}_1}^{\dot{\gamma}_2} k\dot{\gamma}^n - \int_{\dot{\gamma}_2}^{\dot{\gamma}_1} k'\dot{\gamma}^{n'} \quad (2)$$

Where k, k' and n, n' are the consistency coefficients and flow index behavior for forward and backward measurements, respectively.

3. Results and discussion

Rheological properties of SPI solution substantially influence the spinning process and mechanical properties of fibers, as well as casting and film properties. In particular, the rheology of the polymer solution, depending on the concentration and the polymer-solvent interaction, is considered as one of the key factors of the fiber spinning process (Um et al., 2004). We investigated the rheological behavior of SPI solutions to determine the optimum spinning conditions for the wet spinning of SPI filament.

In the urea/sodium sulfite system, SPI solution can flow in the concentration range of 16–20 wt% at ambient temperature.