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Impact of shear force on functional properties of native starch and resulting gel and film

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ABSTRACT

In this study, cornstarch dispersions were physically modified through a high-speed shear homogenizer with various shear-induced rates (56–400/s) and physical, thermal, crystalline and morphological properties of modified starch were investigated. Then, a hydrogel and a soft film were fabricated from the modified starches to evaluate the effect of shear force on their functional properties. Scanning electron microscopy revealed that the shearing treatment altered the shape of granules and changed their surface appearance. This was particularly found to be the case when sufficiently high intensity of shear force was used. X-ray diffraction pattern showed the crystallinity degree of granules decreased after the mechanical treatment. Two endothermic peaks detected on differential scanning calorimetry curves of native sample, whose enthalpy decreased after the treatment. Moreover, swelling power of the starch increased by increasing the shear rate as proven by decreasing the enthalpy of the endothermic peaks. It was found that the shear treatment produced an excellent hydrogel with improved textural parameters and softer structure. The textural analysis revealed a prominent increase in hydrogel hardness with increasing the shear rate, whereas cohesiveness parameter decreased. Atomic force microscopy revealed that the rough hydrogel surface became smooth after the treatment. Regarding the starch-based film, the physico-mechanical results showed that water resistance, water barrier property and tensile strength improved after the shear force treatment.

1. Introduction

Starch is one of the most important and abundant biopolymer, which has a wide range of applications in food industry due to its unique functional properties and relatively low cost (Beadle et al., 1978; Thomas and Atwell, 1999; Chi et al., 2008). It plays an important role in the formulation of food products, either as a raw substantial or as a food additive (Mason, 2009). The starch has a semi-crystalline structure, where its internal zone is non-crystalline and the outer region is crystallized. It is composed of two major subunits, amylose that is linear and slightly branched, and a highly branched fraction named amylopectin (Bemiller, 1997).

The use of native starch in food applications suffers from many drawbacks, including poor melt process-ability (high viscosity) and low solubility in common organic solvents. To make native starches more suitable to use in the food products, they are often modified through physical, chemical and enzymatic methods. The common chemical modification, including derivatization (Kiatkamjornwong et al., 2001), acid-thinning/hydrolytic (Lawal et al., 2005), dextrinization and oxidation (Wolf et al., 1999), the physical one involves irradiation using a high-energy irradiation, hydrothermal treatment, thermo-mechanical treatment (Nayouf et al., 2003; Din et al., 2017) and osmotic-pressure-treatment (Pukkahuta et al., 2008), and finally the enzymatic modification consisting α and β-amylolysis (Hickman et al., 2008). The functional performance of starch through these treatments can be modified in relation to improving its cooking properties (Bemiller, 1997), decreasing starch paste syneresis (Kaur et al., 2012), increasing freeze-thaw stability of starch gel (Lee et al., 2002), as well as improving functional

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properties of starch-based film (López et al., 2008). The chemical and enzymatic methods are often most efficient approaches to improve starch functionality, but they have some drawbacks in practice, including most expensive modifier agents, consumer safety, environmental concerns and time consuming processes (Bemiller, 1997).

A mechanical process based on shear force can be used to modify the functional properties of starch by using a rotor-stator device (Urban et al., 2006; Müller-Fischer et al., 2007). The rotor-stators are a specific class of mixers, which commonly used in food application in order to disperse the solid particles in a continuous phase. They have a blade inside of a stationary perforated tube, rotating at a high speed and quickly shear the samples. The kinetic energy generated by the rotor leads to high-energy dissipation rate in a small volume (Utomo et al., 2009). Thus, these mixers can be used to handle energy intensive processes such as emulsification and homogenization (Maa and Hsu, 1996; Utomo et al., 2009). The produced energy can efficiently break the droplet to the fine particles in the continuous phase. Here, the operative breakup energy is attributed to forces of inertia and shearing in the turbulent flow (Urban et al., 2006). Moreover, the rotation at the high rotor speed makes a shear rate with a slight pressure to draw liquid in/out of the system (Maa and Hsu, 1996).

The effect of shear force on the microstructure of starch is of considerable interest to the food application, since it can change the functional properties of this biopolymer. In the research conducted by Kaur et al. (2013), they found that the shear treatment led to an increase in amylose content and paste viscosities, as well as a decrease in the gelatinization temperatures and size of granules. Wang et al. (2015) showed that shear force could degrade the starch molecule and release its soluble component. They also found that the sheared starch showed a lower enthalpy change and higher stability of hot and cold paste. Farahnaky et al. (2014) reported that degradation of starch molecules at high shear rate was more than that of the gentle ones. Moreover, they reported that application of the shear force at higher temperatures caused a notable decrease in textural properties of the starch gels. On the other hands, there are numerous studies reporting the effect of shear force on other biopolymers with the aim of improving their functional properties such as whey protein concentrate (Simmons et al., 2007), the blend of whey protein isolate-kappa carrageenan (Gaaloul et al., 2009), pectin (Guo et al., 2014) and soy protein isolate (Bi et al., 2014).

The high-speed shear homogenization has advantages of being a simple process, easy-to-operate method with a minimal environmental concern. Since starch is always sheared with other ingredients to produce starch-based products, the intense mechanical shear force may affect its physico-mechanical, structural and thermal properties. Therefore, it is important to study how shearing process may alter the functional properties of the starch, which finally affect the quality of starchy food products. The first priority of the current research was to study the effect of high-speed shear homogenization with various shear-induced rates on the cornstarch granules, whereby physical, thermal, crystalline and morphological properties of the granules would be changed by this treatment. Moreover, the effects of the shear force on the functional properties of the cornstarch hydrogel and its film were also discussed in more detail.

2. Materials and methods

Commercial cornstarch with 7.4% moisture content, 0.6% fat, <1% ash and 26.7% amylose content (AACC, 2000; Morrison and Laignelet, 1983) was purchased from Mahshad CO. (Yazd, Iran). Dimethyl sulfoxide (DMSO), potassium carbonate (K_2CO_3), sodium chloride (NaCl) and glycerol were purchased from Merck (Merck Co. Ltd, Germany).

2.1. High-shear force treatment

The native sample was completely dispersed in deionized water (100 g/L) at an ambient temperature and gently stirred by a magnetic stirrer for 60 min. After that, the starch suspension was physically sheared using a high-speed rotor-stator apparatus (Ultra-Turrax, IKA* T25 digital, Germany) includes a high-speed motor, lifting system, control system and sample container, which was generated shear force with adjustable speeds at different shear rates from 56/s to 400/s. The modified samples were signed as SF_1, SF_2 and SF_3, which implied the treated starch with shear speed at a rate of 56/s (367 G-force), 210/s (5690 G-force) and 400/s (20664 G-force), respectively. The control sample was the native cornstarch without shearing treatment. The shearing treatments were carried out at room temperature with a time constant of 15 min. After completing the treatment, the sheared samples were collected and dried in an oven at 45 °C for 18 h. Next, the dried samples were ground to break the clumps, and filtered through a sieve with a mesh of 170 (88 μm) to reach the appropriate particle size. Finally, the samples were poured into the glass container and stored in desired temperature (4 °C) for more characterization and testing.

2.2. Granules study

2.2.1. Morphological behavior by SEM

The effect of shearing treatments on the morphological structure of the granules was observed using a scanning electron microscope (SEM, Hitachi, S-2830N, Japan). Initially, a tiny amount of freeze-dried samples was sputter-coated with a thin layer of gold/palladium at 20 mA for 4 min (JEOL JFC-1600, Auto Fine Coater, Tokyo, Japan). An acceleration voltage of 20 kV was used to avoid the samples from being damaged with a magnification objective of 3 kX.

2.2.2. Intrinsic viscosity

The intrinsic viscosity was measured by an Ostwald viscometer with a nominal constant of 0.011 (Ubbelohde-type, Germany), equipping with a thermostatic water bath under the precise temperature control (35 ± 0.1 °C). The solvent was prepared by adding 0.9 dL of DMSO to 0.1 dL of deionized water (90% v/v). Various amounts of the starch sample (<1 g/dL) were dissolved in the solvent to cover concentrations of the dilute and semi-dilute regions. Then, the relative viscosity (η_{rel}), specific viscosity (η_{sp}), reduced viscosity (η_{red}) and the inherent viscosity (η_{inh}) were calculated by Eqs. (1)–(4), respectively:

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0}.\frac{\rho}{\rho_0} \quad (1)$$

$$\eta_{sp} = (\eta_{rel} - 1) \quad (2)$$

$$\eta_{red} = \frac{(\eta_{rel} - 1)}{C} \quad (3)$$

$$\eta_{inh} = \frac{Ln\ (\eta_{rel})}{C} \quad (4)$$

where, t, t_o and ρ/ρ_o are the efflux times of solution and solvent and the ratio of solution density to the solvent, respectively. The starch concentration is represented as C.

The intrinsic viscosity was obtained from the extrapolation of reduced and inherent viscosities to infinite dilution according to