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Characterization of starch films containing starch nanoparticles Part 1: Physical and mechanical properties

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ABSTRACT

We report, for the first time, the preparation method and characteristics of starch films incorporating spray dried and vacuum freeze dried starch nanoparticles. Physical properties of these films such as morphology, crystallinity, water vapor permeability (WVP), opacity, and glass transition temperature (T_g) and mechanical properties (strain *versus* temperature, strain *versus* stress, Young's modulus and toughness) were measured. Addition of both starch nanoparticles in starch films increased roughness of surface, lowered degree of crystallinity by 23.5%, WVP by 44% and T_g by 4.3 °C, respectively compared to those of starch-only films. Drying method used in preparation of starch nanoparticles only affected opacity of films. The incorporation of nanoparticles in starch films resulted into denser films due to which the extent of variation of strain with temperature was much lower. The toughness and Young's modulus of films containing both types of starch nanoparticles were lower than those of control films especially at <100 °C.

1. Introduction

Starch-based films have drawn considerable attention due to their potential application in producing agricultural foils, garbage or composting bags, food packaging and edible films (Yun & Yoon, 2010). Starch-based films can be produced by adding judicious amount of plasticizers and using either hot melt processing or solution casting (Bengtsson, Koch, & Gatenholm, 2003; Kampeerapappun, Aht-ong, Pentrakoon, & Srikulkit, 2007; Wilhelm, Sierakowski, Souza, & Wypych, 2003). The addition of plasticizers such as formamide (Dai, Chang, Geng, Yu, & Ma, 2010), sorbitol (Galdeano, Mali, Grossmann, Yamashita, & García, 2009), xylitol (Vieira, da Silva, dos Santos, & Beppu, 2011), glycerol (Kampeerapappun et al., 2007), and glycerol and xylitol in combination (Muscat, Adhikari, Adhikari, & Chaudhary, 2012) considerably improves mechanical properties such as tensile strength, strain at break, flexibility and modulus of elasticity. Even though the presence of plasticizers improves these mechanical properties of starch films, due to hydrophilic nature of starch and its sensitivity to moisture and heat, further modification is usually necessary.

There are many methods that can be used to modify the structure and function of starch-based films. Among these methods, blending with other compounds in the film forming solution is a useful way to modify the structure and properties of starch-based films (Briassoulis, 2004). Many materials such as chitosan (Bourtoom & Chinnan, 2008; Zhai, Zhao, Yoshii, & Kume, 2004), protein (Jagannath, Nanjappa, Das Gupta, & Bawa, 2003; Ryu, Rhim, Roh, & Kim, 2002), polyvinyl alcohol (PVA) (Follain, Joly, Dole, & Bliard, 2005; Jayasekara, Harding, Bowater, Christie, & Lonergan, 2004), and poly-3-hydroxybutyrate (PHB) (Godbole, Gote, Latkar, & Chakrabarti, 2003) have been successfully used to produce starch-based films having some tailored properties.

In addition, a plethora of micro- or nano-particles can be used to blend with the starch suspension to produce starch-based films. Wittaya (2009) reported the preparation method and characteristics of rice starch films reinforced with microcrystalline cellulose from palm pressed fiber. Xiong, Tang, Tang, and Zou (2008) added nano-SiO_2 in starch-based biodegradable film and reported that the tensile strength, elongation at break, and transmittance increased by 79.4%, 18%, and 15%, respectively. Interestingly, the water absorption was found to decrease by 70% due to the addition of nano-SiO_2. Byun, Park, Lim, and Yoon (2011) studied the effect of the presence of nano-sized poly(acrylamide-co-methyl methacrylate) (PAAm-co-MMA) and nano-sized TiO_2 (P-25)/PAAm-co-MMA composite in starch-based films. These authors studied the morphology, crystallinity, physical and mechanical properties, and photocatalytic degradability of the above mentioned films and reported that the presence of micro- and nano-particles significantly affects the physical and mechanical properties.

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However, the formation and characteristics of starch-based films containing starch nanoparticles, to our knowledge, are not reported so far. Starch nanoparticles (StNPs) or nanospheres are nano-sized (1–1000 nm) particulates of starch prepared by chemically cross-linking starch molecules with appropriate cross-linkers (Le Corre, Bras, & Dufresne, 2010). We previously reported that the starch nanoparticles can be successfully produced using the water-in-oil (w/o) mini-emulsion cross-linking technique using a high pressure homogenizer (Shi, Li, Wang, Li, & Adhikari, 2011). Because starch is the major component in both the starch nanoparticle and starch-based films, it is expected that the blending or mixing of starch nanoparticles in starch-based films would be easier than other compounds having dissimilar molecules. Hence, it is expected that the production of starch-based films containing starch nanoparticles would be practicable.

In this first part, we attempted to produce starch films with and without starch nanoparticles and investigate their physical properties such as morphology, amorphous/crystalline nature, WVP, opacity, and glass transition temperature and mechanical properties (strain as a function of stress, Young's modulus, toughness and strain as a function of temperature). Spray dried and vacuum freeze dried starch nanoparticles were incorporated in the starch films to understand the impact of drying methods used to prepare the nanoparticles.

2. Materials and methods

2.1. Materials

Corn starch was obtained from Hebei Zhangjiakou Yujing Food Co. Ltd. (Hebei, China). Glycerol (analytical grade) was purchased from Beijing Chemical Reagent Ltd. (Beijing, China). Xylitol (food grade) was purchased from Tianjin Jinguigu Science & Technology Development Co. Ltd. All these materials were used as received.

2.2. Preparation of starch nanoparticles

Starch nanoparticles were produced following the emulsion cross-linking method using a high pressure homogenizer (Shi et al., 2011). Spray drying and vacuum freeze drying techniques were used to prepare starch nanoparticles (Shi, Li, Wang, Zhou, & Adhikari, 2012; Shi, Wang, Li, & Adhikari, 2012).

2.2.1. Spray drying

A bench-top spray dryer (GPW120-II, Shandong Tianli Drying Equipment Co., Ltd., Shandong, China) with 500 mL/h evaporation capacity was used throughout the spray drying trials. The atomization of the droplet was accomplished using a 0.7 mm two-fluid nozzle and compressed air was used as atomizing medium. The flow rate of the compressed air was 10 L/min and its pressure was maintained at 608 kPa. The feed flow rate and inlet temperature were set at 5.4 mL/min and 100 °C, respectively. The powders were collected at the cyclone and finally transferred to resealable snap lock bags. These spray dried starch nanoparticles were stored in a desiccator containing dried allochroic silica gel at 25 °C.

2.2.2. Vacuum freeze drying

A laboratory-scale vacuum freeze dryer (LGJ-18, Sihuan, China) was used to dry the starch nanoparticles. The sample dishes ($0.1\,m^2 \times 3\,cm$) containing the suspension ($0.1\,m^2 \times 1\,cm$) were placed in the cold trap of the vacuum freeze dryer (−60 °C) for 5 h to ensure complete freezing of the sample. Subsequently, the frozen samples were placed in drying chamber and then the chamber was evacuated (<100 Pa). The temperature of frozen samples was varied from −30 °C to 45 °C step by step in the 28 h-long drying period (1 h each at −30 °C, −25 °C, −20 °C, −15 °C, −10 °C, −5 °C; 2 h each at 0 °C, 5 °C, 10 °C, 15 °C, 20 °C, 25 °C, 30 °C, 35 °C, 40 °C and finally 4 h each at 45 °C). The vacuum freeze dried starch nanoparticles were stored in the same desiccator in which spray dried samples were stored.

2.3. Film preparation

7.0 g of previously dried (40 °C for 6 h) cornstarch and 3.0 g of plasticizers (glycerol and xylitol, 1:1) was added into 200 ml deionized water to form starch-plasticizer dispersions with 5.0 wt.% (w/v) solid concentration. The dispersion batches were thoroughly stirred at 300 rpm (in beakers) for 1 h using a thermostated water bath in boiling condition. Evaporation was minimized by covering the beakers with six layers of water resistant films. After gelatinizing the starch at 100 °C for 1 h and cooling to 70 °C, 0.5 wt.% (w/v) starch nanoparticles was added into the dispersions (Fu, Wang, Li, Wei, & Adhikari, 2011). These dispersions, after introducing the starch nanoparticles, were further stirred for 30 min at 300 rpm. The dispersions having no starch nanoparticles in them severed as the control sample.

Films were cast by syringing 8 mL of the above mentioned dispersions into 9 cm diameter polycarbonate petri dishes. Films were dried for over 8 h at 45 °C. All the dried starch film were preserved in a humidity chambers (25 °C, RH = 53%) for further testing. The nomenclature of these films is presented in Table 1.

2.4. Physicochemical properties

2.4.1. Morphology

Film surface morphology was examined using a scanning electron microscope (S-3400N, Hitachi Instruments Ltd., Japan). Films were firstly dried at 100 °C for 12 h. Then these dried film samples were mounted on stub with double-sided adhesive tape and coated with a thin layer of gold. The surface characteristics of the samples was observed and recorded under S-3400N using an accelerating voltage of 15 kV and a 5000× magnification.

2.4.2. X-ray diffraction (XRD)

The amorphous/crystalline structure of the sample was examined using an X-ray diffractometer (XD-2, Beijing Purkinje General Instrument Co., Ltd., China). It used nickel filtered Cu Kα radiation ($\lambda = 0.15406$ nm) and worked at a voltage of 36 kV and current of 20 mA. The slit width of 1° and the 2θ range from 5° to 45° in steps of 0.02°/s were used. The starch film samples were cut into pieces and pulverized using a laboratory grinder. The pulverized sample was further dried in a laboratory oven (105 °C) for 6 h to remove the moisture. The dried powder sample was compacted to form an even surface before loading to the XRD instrument. The temperature and relative humidity (RH %) for tests were 25 °C and 20%, respectively.

2.4.3. Water vapor permeability (WVP)

The ASTM method E96-80 with some modifications (ASTM, 1987) was used to measure WVP of the films. Each film sample was sealed over a circular opening (area = 0.000632 m^2) in a permeation cell that was conditioned at 25 °C in a desiccator. As outlined in the standard method, anhydrous calcium chloride (0% RH) was placed inside the cell while a saturated sodium chloride solution (75% RH) was placed in the desiccator. Due to the vapor pressure gradient across the film, the water vapor continuously diffuses through the film and the water vapor transmission rate can be determined from the weight gained by the permeation cell. The change in the weight of the cell was measured every 24 h over a week.

The change in the weight of the cell was plotted as a function of time and the slope of each line was calculated by linear regression. The water vapor transmission rate (WVTR) was calculated from