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Preparation and characteristics of oxidized potato starch films

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ABSTRACT

Starch films were developed from oxidized potato starch (OPS) with glycerol as a plasticizer at different contents. The OPS films were transparent and flexible. The mechanical properties of these films were measured, and the results indicated that the film with 19.4% glycerol exhibited the desirable mechanical properties. X-ray diffraction study showed that the increase of glycerol content led to a decrease in the crystallinity for OPS films, and storage conditions such as storage time, storage temperature and relative humidity also had certain effects on the retrogradation of starch owing to re-crystallization. Anti-leakage, anti-crosslinking, and stability in acid or alkali solutions of the OPS films were also studied, and the results indicated that the OPS films had excellent anti-leakage ability for vegetable oil, good anti-crosslinking ability in saturated formaldehyde vapor, and good stability in acid aqueous medium, but poor stability in alkali aqueous medium.

1. Introduction

Plastics have been widely used in daily life because of their light, inertness, transparency, comparatively high mechanical properties and low cost. Nowadays, about 150 million tons of plastics are produced annually all over the world. An increase in plastics production would result in an increase of oil consumption because most of these products are based on crude oil. Moreover, plastics products can cause serious environmental pollution because most of the plastics products are not degradable in the normal environment. Landfills are the dominant disposal sites for waste plastics, and this would take too much land (Kim, 2003; Okada, 2002; Parra, Tadini, Ponce, & Lagão, 2004). Therefore, synthetic or natural biodegradable polymers have been a major focus of interesting, especially the use of natural polysaccharides such as cellulose, chitosan and starch et al. These polysaccharides are biodegradable, renewable and edible, which makes them ideal food packaging materials (Pavlath & Robertson, 1999; Tanada-Palmu & Grosso, 2003).

Film from edible natural polymer is one of the important packagings. It is primarily used to extend the shelf-life and quality of foods by preventing changes in aroma, taste, texture or handling characteristics (Tharannthan, 2003). The film can provide additional nutrient content and enhance sensory characteristics, and may be consumed along with food. The films, primarily composed of polysaccharides or proteins, have suitable mechanical and optical properties, as well as good gas barrier properties for such as O_2 and CO_2 for coating applications, but they are highly sensitive to moisture and show poor water vapor barrier properties (Petersson & Stading, 2005; Romero-bastida et al., 2005; Zamudio-Flores, Vargas-Torres, Pére-Gonzálea, Bosquez-Molina, & Bello-Pérez, 2006).

Starch, as one of the most important and abundant polysaccharides in nature, has been the subject of numerous researches. It is widely used in industry to provide functional properties such as gelling, thickening, bonding and adhesion. It has been also extensively used in non-edible or edible film preparations (Soares, Lima, Oliveira, Pires, & Soldi, 2005).

Starch is a high M_w polymer of a hydro-glucose units linked by α-D-glycoside bonds. Starch molecules usually contain linear amylose and branched amylopectin. Amylose has a smaller M_w, and amylopectin has a larger M_w of 50–500 million (Maurer Hans, 2001). However, amylose is responsible for the film-forming capacity (Romero-bastida et al., 2005). Starch from various sources presents different amylose/amylopectin ratios or M_w, which can induce distinct properties. The films of high-amylose corn starch or potato starch was more stable during aging, lost little of their elongation and had not or a slight increasing in tensile strength (Krogars et al., 2003; Lawton, 1996). Films from cassava starch had good flexibility and low water permeability, indicating potential application as edible films (Parra et al., 2004). Petersson & Stading (2005) reported starch films from three different sources and found that there was not significant difference in tensile strength value between mango and okenina starch films prepared by thermal gelatinization method; however, banana starch films had the highest tensile strength value. Yam starch was also used to prepare films (Mali, Grossmann, García, Martino, & Zaritzky, 2005a, 2004).

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Pure native starch films are brittle compared with synthetic polymers such as polyethylene, and usually need to be plasticized. The most effective plasticizers should generally resemble most closely to the structure of the polymer that they plasticize. Thus, the most commonly used plasticizers in starch-based films are polyols, such as sorbitol and glycerol. The addition of these plasticizers can avoid cracking of the film during handling and storage (Arvanitoyannis & Biliaderis, 1998), affect gas, water vapor and solute permeabilities (García, Martino, & Zaritaky, 2002a, 2002b), as well as sorption characteristics. Laohakunjit and Athapol (2004) reported the effect of plasticizers on mechanical and barrier properties of rice starch film. They found that glycerol-plasticized films showed a larger water vapor transmission rate, a higher solubility and a higher elongation, but a lower tensile strength than that of sorbitol-plasticized films. While, at 30% and 35% concentration, sorbitol-plasticized films exhibited lower oxygen transmission rate than that of glycerol-plasticized films.

Water is also an effective plasticizer for polysaccharide materials, and plays a significant role for the properties of starch film. With the increased water content, the starch film showed both an increased strain and stress at break (Hulleman, Janssen, & Feil, 1998; Parker & Ring, 2001). Starch films tend to absorb large quantities of water at elevated relative humidity (RH) conditions owing to their inherent hydrophilic nature. The overload of water could make the starch film unstable. Glycerol films adsorbed faster and more water during storage by comparing with sorbitol films. So appropriate selection of plasticizers and their concentration would be helpful in controlling moisture content and moisture adsorption rate of a starch film, and can improve the stability of starch film under varied RH conditions (Mali, Sakanaka, Yamashita, & Grossmann, 2005b).

Although the functional, organoleptic and mechanical properties of starch films can be modified by the addition of various chemicals in certain amounts (Mali et al., 2005a; Romero-bastida et al., 2005), it is undesirable as an edible film. People prefer to modify the properties of film by improving the properties of starch itself, so many modified starches have been come out. The films made from modified starches exhibited different properties. Crosslinking of starch reinforced the film by chemical bonds that act as bridges between molecules, and it was proved to be a valuable way for providing maximum film strength (Wurzburg, 1987a). Thus, crosslinked starches were used in the preparation of starch xanthates as ion-exchangers for water treatment, stilt materials for microencapsulated coatings and anti-blocking agents for film in the food, textile and paper industry (Kim & Lee, 2002; Wurzburg, 1987a).

Hydroxypropyl (HP) starch is another chemical modified starch. Hydroxypropyl groups are hydrophilic and influence the interaction of starch molecules. A direct comparison of films from hydroxypropylated pea, potato and maize starches showed that there were no differences between the starch varieties in terms of tensile strength or elongation. Lower elongation implied poor and unsuitable usage as coatings or packaging films (Vorwerg, Dijksterhuis, Borghuis, Radosta, & Krōer, 2004).

Oxidized-starch is widely used in industries to provide surface sizing and coating property. Although the main outlets for oxidized-starch are in the paper and textile industries, its application in the food industry is increasing because of its low viscosity, high stability, high transparent, excellent film-forming and binding properties. However, its application as a kind of package materials in the food industries, especially as an edible film, offers a larger space needed to fill. Hydroxyl groups on starch molecules are first oxidized to carbonyl groups and then to carboxyl groups (Wurzburg, 1987b). Therefore, the numbers of carboxyl and carbonyl groups on oxidized-starch indicated the level of oxidation and affected the properties. Zamudio-Flores et al. (2006) reported a starch film prepared with different oxidized banana starch. They found the tensile strength was increased with the degree of oxidation. They thought the presence of carboxyl and carbonyl groups in the oxidized-starch might produce hydrogen bridges with the OH groups of the amylose and amylopectin molecules, and these linkages gave more structural integrity in the polymeric matrix that increased the tensile strength. However, the value of the tensile strength of oxidized banana starch film was near 8 MPa, and it was lower than that of oxidized potato starch film made in our lab.

The native potato starch has higher tensile strength because of its higher M_w, which makes its paste had a high viscosity. So it is impossible to confect potato starch paste with high starch content, which would result in a lower efficiency in film-making. Beside, the transparence of native potato starch paste was poorer than that of oxidized potato starch. So we chose oxidized potato starch (OPS) to prepare edible film, since it had both lower viscosity and higher transparence. Moreover, the higher the oxidized degree was, the lower viscosity and the higher transparence were obtained. While, our primary experiments found that the film from high-oxidized potato starch was crisp and apt to crack, and the low-oxidized potato starch could form a flexible and transparent uniform film. So this paper will study the mechanical, stability and acid/alkali resistant properties of lower-oxidized potato starch films with glycerol as plasticizer, in order to evaluate their application as edible packagings.

2. Materials and methods

2.1. Materials

Potato starch and oxidized potato starch (OPS) were obtained Tianjin TingFung Starch Development Co. Ltd., Glycerol was purchased from Tianjin Yingda sparseness & noble Chemical factory; Polyethylene glycol 400 (PEG), sodium hydroxide, and hydrochloric acid were purchased from Tianjin Chemical Reagent Co. Ltd., Soybean oil was from Northsea Oils and Grains Industries (Tianjin) Co. Ltd.

2.2. Preparation of starch films

OPS films were prepared as follows. Starch slurry was first prepared from a dispersion of 10 g OPS in 100 ml distilled water containing a certain amount of plasticizer-Glycerol. The suspension was preheated at 45 °C for about 30 min in water-bath and gelatinized at 85 °C for about 3 h, and then it was cast on the stainless-steel plate (26 × 18 mm), and dried at 45 °C for about 8 h to get transparent OPS films.

2.3. Mechanical properties

The mechanical properties include the tensile strength (TS) and percent elongation at break (%E). Three or more specimens, with a size of 100 × 15 mm, were cut from each kind of OPS films. The samples were conditioned at 25 °C and 53% RH (a saturated $Mg(NO_3)_2$ solution) for 24 h, and the thickness of the samples was measured with a micrometer before test. Measurements were taken at five different positions for each sample and the average value of these determinations was calculated. This average value was used to calculate the cross-sectional area of the samples (the area is equal to the thickness multiplied by the width of each samples). The tensile strength (TS) and percent elongation at break (%E) were measured using a materials testing machines (The Testometric Company Ltd., United Kingdom) with 10 kg load cell, according to ASTM Standard Method D882-88 (ASTM, 1989). Initial grip separation was 40 mm and cross-head speed was 5 mm/min. The ten-