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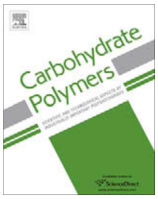

Preparation and characteristics of oxidized potato starch films

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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 tensile strength was calculated by dividing the maximum force exerted on the film during fracture by the cross-sectional areas. Percent elongation at break was expressed as percentage of change of the original length of a specimen between grips at break.

2.4. Solubility in water

Solubility (SW) of the film in water was measured according to literature (Romero-Bastida et al., 2005). The initial weight (M_0) of dry sample, with a size of 40×20 mm for each film, was determined after dried to a constant weight at 40 °C in a vacuum oven. The weighed sample was immersed in beaker filled with 50 mL distilled water. The beaker was sealed to prevent from dust and the evaporation of the water, and stayed at 25 °C for 24 h, during which time the water was periodically wobbled slightly. The sample was taken out and dried to a constant weight at 40 °C in a vacuum oven, and then it was weighed (M_2). The solubility of the sample was calculated as follows:

$$\mathrm{SW}(\%) = 100\% \times (M_0 - M)/M_0$$

Where, M_0 and M were the dry sample weight before and after the test, respectively. For each OPS film, tests were performed in triplicate, and average value was used.

2.5. Moisture absorbability from atmosphere of different saturated humidity

Moisture absorbability (%M) of OPS films was measured under different relative saturation humidity: 33%RH, 53%RH, and 75%RH. Each initial weight (M_0) of dry samples with a size of 40×20 mm was determined after dried to a constant weight at 40 °C in a vacuum oven. The weighed samples were separately laid in incubators with different saturated salt solutions at 25 °C until the weight of each sample became constant. Then the samples were taken out to determine the weight (M) of each sample. Test was performed in triplicate for a OPS film and each moisture absorbability value was calculated as follows:

$$\%M = 100\% \times (M_0 - M)/M_0$$

Where, M_0 was initial weight of dry sample and M was the weight after the test, respectively.

2.6. Swelling capacity in water

Swelling capacity (Swe) of starch film in water was measured in distilled water. The initial weight (M_0) of a dry sample with a size of 40 mm×20 mm was determined after drying to a constant weight at 40 °C in a vacuum oven. The weighed sample was immersed in beaker filled with 50 mL distilled water. The beaker was sealed to prevent from dust and the evaporation of the water, and stayed at 25 °C for 24 h. The sample was taken out and dried to a constant weight at 40 °C in a vacuum oven, and then it was weighed (M). Tests were performed in triplicate and each value of swelling capacity was calculated as follows:

$$\mathrm{Swe}(\%) = 100\% \times (M - M_0)/M_0$$

Where, M_0 and M were the initial weight and the weight of swelled sample, respectively.

2.7. Anti-permeate ability for oil

Anti-permeate for oil of OPS film was measured as follow: 5 ml soybean oil was put into a glass test tube (interior diameter: 30 mm; and outer diameter: 32 mm), and then OPS film, with a size of 50×50 mm, was put and pressed tightly on the open end to seal the tube. The tube was upside down and put on the filter paper on the glass slide, and then we viewed if soybean oil could permeate through the starch films as time went.

2.8. Anti-crosslinking capacity in saturated formaldehyde vapor

The OPS film and gelatin film, as a control, were cut into rectangle samples of 100 mm long and 15 mm wide. The samples were put into the saturated vapor of formaldehyde solution formed in a container and stayed for several days, during which time three OPS and three gelatin samples were taken out at 0 h (immediately), 12, 24, 36, 48 and 60 h, respectively, and the tensile strength (TS) and percent elongation at break (%E) were measured using a materials testing machines (The Testometric Company Ltd. United Kingdom) to compare the anti-crosslinking ability of the OPS film and gelatin film in the saturated vapor of formaldehyde solution.

2.9. Stability in acid or alkali solution

Stability in acid or alkali solution of oxidized-starch films was measured as follows: oxidized-starch films, with a size of 40×40 mm, were immersed in containers filled with 100 mL 0.1 mol/L sodium hydroxide standard solution or 100 ml 0.1 mol/L hydrochloric acid standard solution, respectively. The containers were sealed and stayed at 25 °C for some time, during which the containers were periodically and slightly shaken, and the changes of sample appearance were recorded by digital camera, in order to evaluate the stability of OPS films in acid or alkali solution.

2.10. Dissolving out of small molecules from oxidized-starch films

Dissolving out of small molecules from oxidized-starch films was measured as follows: the oxidized-starch films, with a size of 20×20 mm, were immersed in containers filled with 20 mL PEG-400 or 20 ml soybean oil, respectively. The containers were sealed and stayed at 25 °C for 35 days, during which time the containers were periodically and slightly shaken. Then, the samples were removed and the infrared spectra of the left PEG or soybean oil were taken to analyze the dissolving out of small molecules in OPS films into PEG (400) or soybean oil. IR spectra were taken with an infrared spectrometer (NICOLET560, ThermoNicolet, America) in the wavenumber region of 440–4000 cm^{-1}.

2.11. X-ray diffraction analysis

The X-ray diffraction spectra of starch films were measured using an X-ray diffractometer (X'pert, PANAlytical, Netherlands) with a reference of target: Co Ka radiation ($\lambda = 1.73$ Å), voltage: 45 kV, current: 30 mA. The films were measured at an angle range from 10 to 40° (2θ) with steps of 0.0037° and a measuring time of 5 s/step.

2.12. Transparence of starch films

The transmittance of OPS films was measured with UV–visible spectrometer (Cary50, Varian Inc. America) in the wavenumber region of 200–900 cm^{-1}.

3. Results and discussion

3.1. Mechanical properties of OPS films

Mechanical property is one of the most important parameters to evaluate polymer films, especially for those used as packaging materials, since only strong enough films can undergo high external forces and protect inner articles perfectly. Fig. 1 showed the

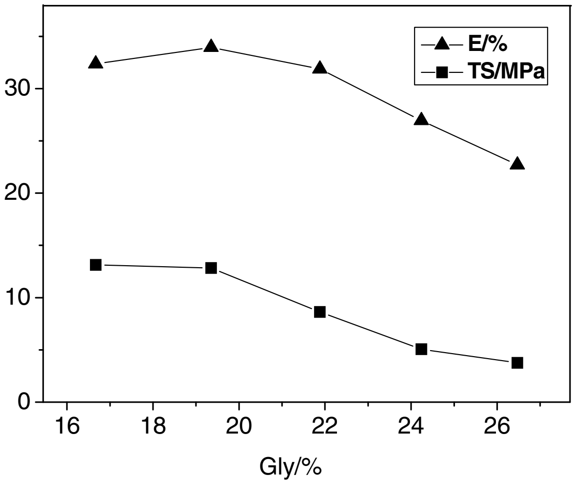

Fig. 1. TS and E% of oxidized potato starch films with different glycerol contents.

changes in tensile strength (TS) and percent elongation at break (%E) of oxidized-starch films with respect to the content of plasticizer-Glycerol. The TS of the OPS films monotonically decreased with the increase of glycerol content, while the %E first increased and reached a maximum value, and then decreased. The maximum value of 31.95% was obtained when the glycerol content was 19.4%, at which the TS of OPS film was 12.82 MPa, slightly lower than the highest value that could be obtained in our experiments, but more than the minimum value (10 MPa) of LDPE required by GB/T 4456-1996. This implied that the OPS film could meet the desirable TS as a packaging material. Ryu, Rhim, Roh, and Kim (2002) had once studied the tensile strength and elongation at break of the high-amylose corn starch films, and they found the similar trends in mechanical properties. The tensile strength of the films decreased as the concentration of glycerol increased; however, the elongation at break increased to a maximum at 60 wt% glycerol and then decreased with further increase in glycerol. Parra et al. (2004) found that the cassava starch films, with more than or less than starch:glycerol ratio of 1:1, presented lower tensile strength.

The %E value of polymeric materials depended on the flexibility of the molecular chain. During the processing of OPS film, the granular and crystal structure of starch were mostly destroyed by high temperature and shear force, and became mainly amorphous phase. This was favorable to the pervasion of plasticizer into the matrix. The permeated glycerol molecules could further decreased the interactions (intra and intermolecular) among the starch macromolecules, because of the formation of hydrogen bonds between hydroxyl groups of starch macromolecules and glycerol small molecules. These all were favorable to the movement and rearrangements of the macromolecule chains of starch, which caused the increase of flexibility of starch films. Therefore, the %E value of starch films increased, while the tensile strength decreased. However, when the glycerol content was further increased, some weakness in structure could be developed. These disadvantages resulted in a sharp decline in the strength, as well as a decline in elongation at break. Mali et al. (2005a) recently studied yam starch films, and found that the tensile strength decreased with increased glycerol. He explained that when glycerol was incorporated in a starch network, direct interactions and the proximity between starch chains were reduced, thus decreased tensile forces, movements of starch chains were facilitated.

3.2. Solubility in water

Fig. 2 showed the changes of solubility (SW) of oxidized potato starch films in water. The SW of the OPS films increased as glycerol increasing. However, the SW value, from 22.77% to 29.86%, did not show a linear increase with increased glycerol content. By comparing the SW value and glycerol content, we found that the former is higher than the later. So the dissolved part, which diffused from starch films, must include molecules from both oxidized potato starch and glycerol. Romero-Bastida et al. (2005) had once reported that the gelatinization method had a remarkable effect on the water solubility of the films. In the case of thermal gelatinization, addition of plasticizer increased water solubility, although the values were all lower than that of the films prepared with cold gelatinization. Water solubility values of OPS films at different glycerol content in this work were similar to the values of films prepared with the thermal gelatinization.

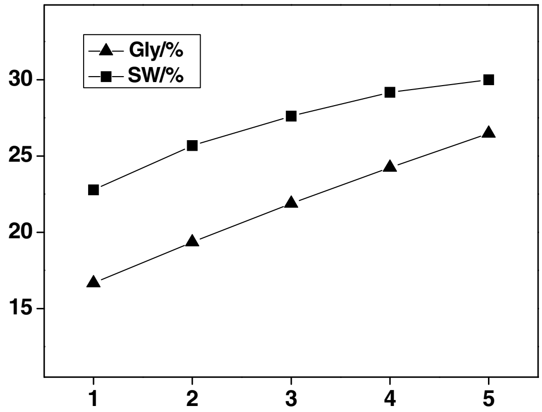

Fig. 2. SW of OPS films with different glycerol contents.

3.3. Swelling capacity of OPS films in water

We studied the changes of swelling capacity (Swe) of OPS film in water. The Swe value didn't show any significant changes with the increased glycerol. The OPS films could absorb 80 wt% water when they were immersed in water, and the value was nearly unaffected by the glycerol concentration.

3.4. Moisture absorbability from atmosphere of different humidity

Moisture absorbability (%M) of OPS films in different relative saturated humidity was shown in Fig. 3. From the illustration, we could find that moisture absorbability of OPS films increased with the increase of glycerol content, when the films were under a spe-

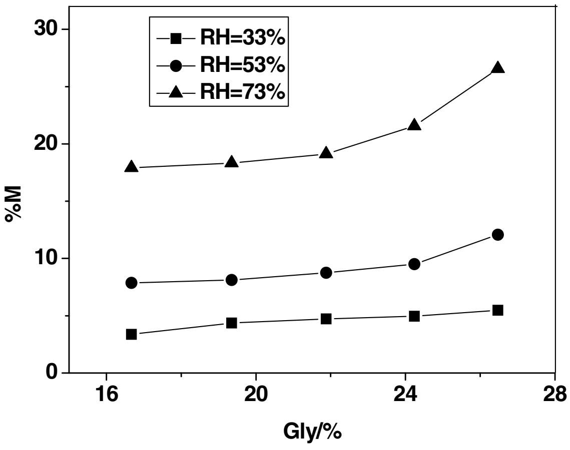

Fig. 3. Moisture absorbability of OPS films in different RH.

cific relative saturation humidity circumstance. Under lower relative humidity of 33%, the %M change, from 3.39% to 5.49%, was not obvious with increased glycerol content. However, the change of %M was much obvious (from 19.4% to 26.6%) under high relative humidity of 73% when glycerol content was over 22%. Under a fixed glycerol content, %M of OPS films grew with the increase of the relative saturated humidity. The higher the relative saturated humidity was, the higher the %M value was obtained. Comparing the three curves in Fig. 3, we found that the changes of %M values were more obvious from RH53 to RH73 than that from RH33 to RH53, though the interval of relative humidity was the same in the two groups. Generally, the water content was kept in equilibrium between the OPS films and the ambient. When films contained more moisture than that of surrounding, the films would send out moisture to surrounding; on the contrary, the film would absorb moisture from surroundings. So, when the films were in higher humid circumstance, they would absorb more moisture.

The addition of glycerol did a more favor to the moisture absorbability of films, because glycerol had excellent water-retaining ability. Besides, the addition of glycerol decreased the interactions among starch-starch macromolecules, so facilitated the absorption of water from the surrounding. This brought about the increase of moisture absorbability of OPS films with the increase of glycerol content.

3.5. Anti-permeate ability for oil

The oxidized-starch films should be anti-permeate for oil. Otherwise, oil would exude through starch films, when the OPS films were used to enclose oily articles or liquid oil containing articles. This might possibly causes leakage of wrapper, and also affects the appearance, flavor, and properties of the articles. So it is necessary to study it. The tubes, containing soybean oil, were covered with OPS films, and inversely put on the filter paper for 100 days at room temperature and humidity. This could help us to view if the oil can pass through the starch films and blot the filter paper. The results showed that the soybean oil did not show any trace of permeating through the starch films with different glycerol contents. Actually, OPS starch films have many oleophobic (or hydrophilic) hydroxyl groups and carboxyl groups, these groups can prevent the adsorption of oil molecules on the film surface. So the films offered good anti-permeate for oil.

3.6. Stability in acid or alkali solution

The oxidized-starch film, as a packaging material, was natural and edible. However, when it was used as packing material, the wrapped article might be a little bit of acid or alkali. These might affect the stability of starch films, so here we studied the stability of starch films in acid or alkali solution. The results were shown in Figs. 4 and 5. When the OPS film was immersed in 0.1 mol/L hydrochloric acid solution, it had a slight size increase from 40 × 40 mm (Fig. 4a) to 43 × 43 mm (Fig. 4b). But this trend did not go further from the 2nd day (Fig. 4c). After 60 days, the film still retained integrity, only some micro-cracks on the surface were found though microscope (Fig. 4d). This implied that OPS film could endure acidic condition. However, the OPS film showed an obvious swelling at 4 h (Fig. 5a) in 0.1 mol/L sodium hydroxide solution. The film began to crack at 1 day (Fig. 5b), and disintegrated completely at 3 days (Fig. 5c). With the time going, the fragments became smaller and smaller, and ultimately dissolved completely in alkali solution at 30 days (Fig. 5m). Sodium hydroxide had once acted as active agent to treat starch before the chemical modification of starch, in order to improve the reacting activity of starch molecules. Sodium hydroxide could combine with the un-oxidized hydroxyl on oxidized-starch molecules, partly destroy the hydrogen bonds and decrease the interactions (intra and intermolecular) among the starch macromolecules. All these facilitated the swelling and gelatinization of starch. Moreover, sodium ions could react with carboxyl to form carboxylate, and this would increase the hydrophilicity and solubility of starch. The above reasons explained why OPS films gradually disintegrated and dissolved in the alkali condition. The above experimental results suggested that the OPS film can be used as packaging material for acidic articles, but it is not suitable for alkali articles.

3.7. Dissolving out of the small molecules from oxidized-starch films

Since the OPS films used glycerol as plasticizer, the small molecules might transmit from film into the wrapped articles when the film is directly contacted with articles. This would cause the contamination of the articles. At the same time, the film maybe became brittle because of the loss of plasticizer, so we studied the dissolving out of the glycerol molecules from the starch film into the soybean oil as a hydrophobic medium and into PEG as a hydrophilic medium. By comparing the infrared spectra (shown in Fig. 6) of pure PEG and PEG after dissolving out experiment, we found that there was an obvious increasing in both intensity and width for hydroxyl peak of PEG after dissolving out experiment, and the wave numbers moved from 3358.62 cm^{-1} (pure PEG) to 3385.18 cm^{-1} (PEG after dissolving out experiment). The experimental results implied that glycerol molecules partly dissolved out from oxidized-starch films when the OPS film was immersed in PEG (400). However, it didn't show any differences between the infrared spectra of pure soybean oil and soybean oil after dissolving out experiment, which implied the glycerol molecules did not show obvious dissolving out from starch films into soybean oil. At the same time, we have viewed the weight and the appearance changes of OPS films during the test. After the film was immersed in PEG medium for 35 days, its weight decreased by 7.8% (the glycerol content in films was 19.4%), and the film became unyielding and brittle. The experimental results confirmed that glycerol molecules partly dissolved out from oxidized-starch films when the OPS film was immersed in PEG (400). However, the weight of film, immersed in soybean oil for 35 days, did not show any decrease, but slightly increased(about 0.03%), and the appear-

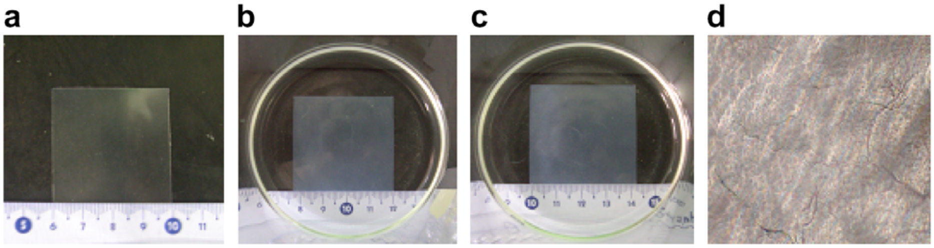

Fig. 4. Digital photos of the oxidized potato starch films in acidic condition. (a) before test, (b) 1 day, (c) 60 days, (d) magnified photo of (c).

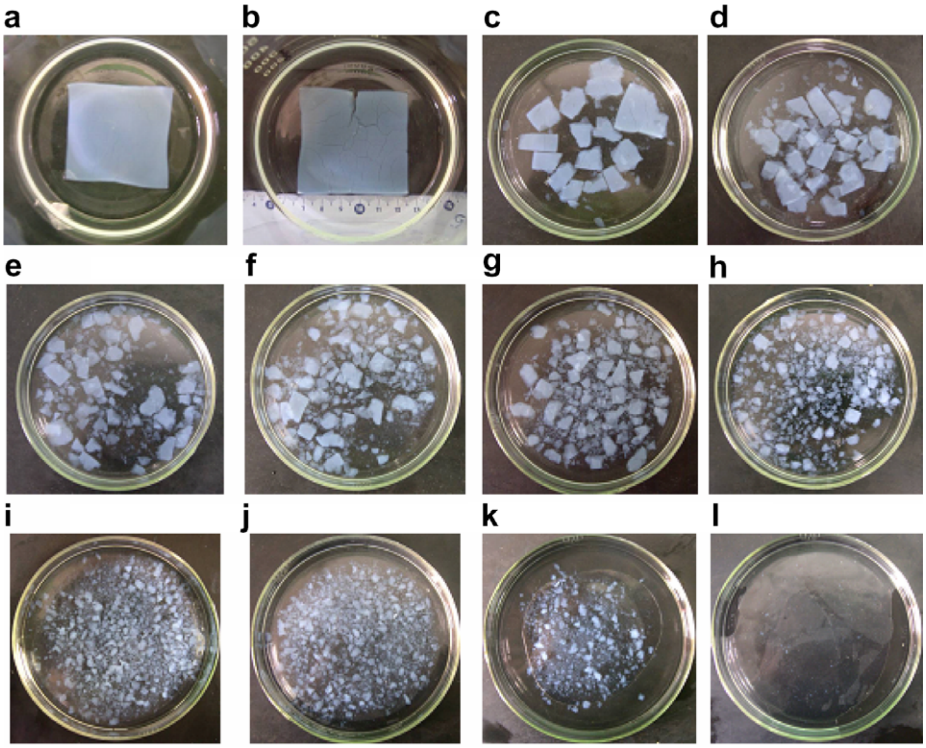

Fig. 5. Digital photos of the oxidized potato starch films in alkali condition. (a) 4 h, (b) 1 day, (c) 3 days, (d) 5 days, (e) 7 days, (f) 10 days, (g) 13 days, (h) 16 days, (i) 19 days, (j) 22 days, (k) 26 days, (l) 30 days.

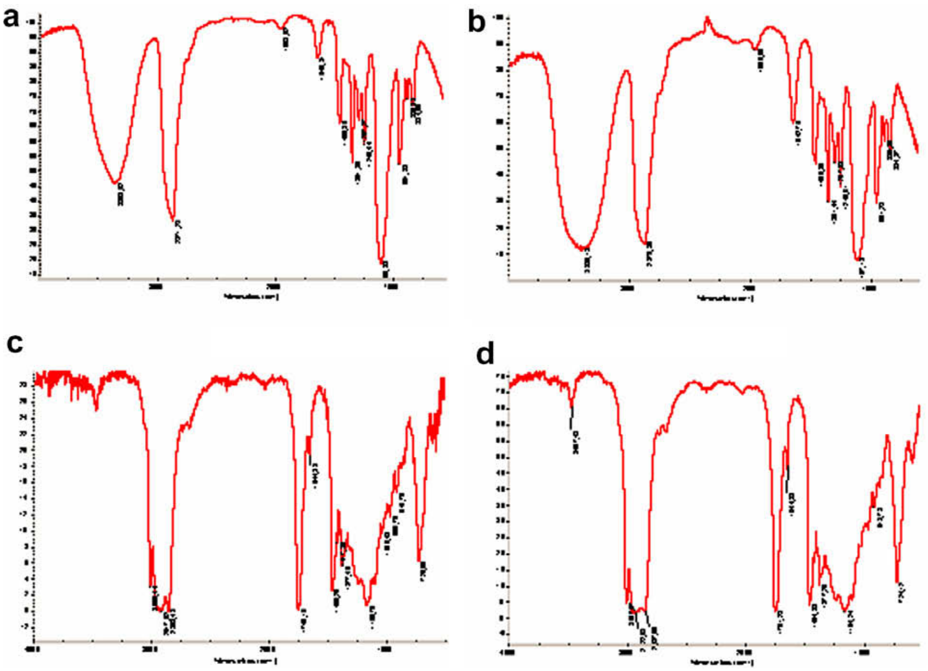

Fig. 6. IR spectrum of (a) pure PEG, (b) PEG medium contacted with OPS film, (c) pure soybean oil, (d) soybean oil contacted with OPS film.

ance was unchanged. The increase of weight might be caused by the attachment of soybean oil on the surface of film, which was hard to clean completely. The above experimental phenomenon implied that the OPS film was favorable for using as a packaging material for oil contained articles, and could guarantee the ingredients of both articles and films itself unchanged.

3.8. X-ray diffraction analysis

Native starch granule is semi-crystalline and shows different crystalline patterns (A–C, and V) according to sources. The A-, B-, and C-type crystals consist of packed double helix, while V-type conformation is a single helix structure resulting from amylose complexed with some components such as water, iodine, butanol and fatty acid (Krogars et al., 2003).

The X-ray diffraction of oxidized-starch films with different glycerol content is shown in Fig. 7. The increase of glycerol content resulted in a decreased crystallinity of starch films, which was favorable to the flexibility of films. Cyras, Zenklusen, and Vazquez (2006) studied the crystallinity of esterified starch films with different glycerol contents and found the similar results. By comparing the X-ray diffraction patterns of the oxidized-starch film and the oxidized-starch granule, we found that the intensity of peaks for films was lower than the intensity for starch granule, although the location of peaks almost the same. This implied that the gelatinization and addition of glycerol did not change the crystal pattern of the starch, but decreased the crystallinity. During the gelatinization, the crystalline regions of starch granules were obviously destroyed by heating and mechanical stir, and the permeation of glycerol could strengthen this destruction. Generally, the remained crystalline particles could act as nucleus to induce the re-crystallization during cooling stage, and the crystallinity might be re-growth again. Actually, the added glycerol blocked the rearrangement of starch segments and prevented the growth of crystal on nucleus by forming strong hydrogen bond with hydroxyl groups on starch chains. As a consequence, the crystallinity of starch films decreased.

For starch film, the re-crystallization of starch macromolecules during the storage is one of the reasons that make the film become brittle, called retrograde. We studied the changes of X-ray diffraction pattern of starch films stored at 53%RH under different temperature. By Comparing the X-ray diffraction pattern at 2, 25 and 40 °C, we found that the area of crystalline peaks increased slightly with the time under any storage temperature. This means that the crystallinity of the OPS films increased gradually compared with fresh OPS film. However, this crystallinity change was different under different temperature. At 10th day, the peak at $2\theta = 17$ became obvious when the films were stored at 2 or 25 °C. But this phenomena happened at 5th day when the films were stored at 40 °C, although the difference in crystallinity at 35th days was not obvious under different temperature. The results implied that the films were stable under normal conditions.

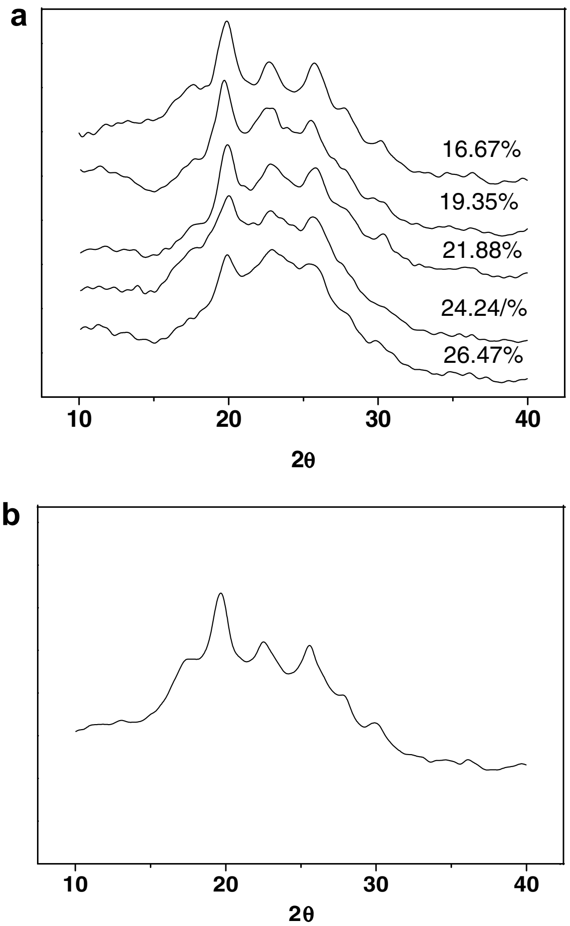

Fig. 7. X-ray diffraction of (a) oxidized-starch films and (b) oxidized potato starch granule

During the storage of the films, humidity was another important factor need to be considered. So we studied the change of the X-ray diffraction pattern of OPS films stored at different relative humidity at 25 °C. In comparison, we found that the area of crystalline peaks under different relative humidity had the same trend, which increased slightly with the time and became more obvious at 35th day. At 10th day, there was not significant difference in crystallinity under different relative humidity. But at 20th day, the peak at $2\theta = 17$ was more obvious when the films stored at 73%RH than that at 53%RH, but the difference between 53%RH and 33%RH was slight. And at 35th day, the peak was even more obvious at 73%RH than that at 33%RH and 53%RH, although no obvious difference was observed in the peaks at 33%RH and 53%RH. At high relative humidity, starch films absorbed more water molecules. This made the segments motion of starch chains easier, which is favorable for the rearrangement of starch segments onto the nucleus. The OPS films had a prominent trend to recrystalize at high relative humidity. The above results implied that the film should not keep in high humidity circumstance.

3.9. Anti-crosslinked ability in saturated formaldehyde vapor

One of the drawbacks for the protein film, such as gelatin film, is the unstable property during storage. When protein films contacted with formaldehyde in the air, the formaldehyde molecules could act as crosslinking agent to crosslink the protein macromolecules, resulted in decrease in flexibility. So anti-crosslinked ability of the OPS films was investigated. The changes of tensile strength and the percent elongation at break of OPS films in saturated formaldehyde vapor for different hours were shown in Fig. 8(a). We chose the films with 19.4% glycerol to view the anti-crosslinked ability, because it exhibited the optimal mechanical properties according to the above discussion. The experimental results showed that both tensile strength and percent elongation at break didn't show obvious changes, although the films have stayed in the saturated formaldehyde vapor up to 60 h. This implied that the oxidized potato starch films could hardly crosslink with formaldehyde molecules in air. This was dramatically different from gelatin films as shown in Fig. 8(b), which was easily deteriorated owing to crosslinking reaction with aldehyde molecules. Once crosslinked, the film had a low flexibility and water solubility. The results told us that OPS films have a better anti-crosslinked ability than that of protein films.

3.10. Transparence of films

The oxidized potato starch films formed by casting method were transparent and homogeneous. The OPS films had comparatively high transmittance (T), about 80% transmittance in visible light district, and the glycerol content did not show any significant effect on the transmittance of the films. The above films had a thickness of 300 μm that is much thicker than that of normal PE

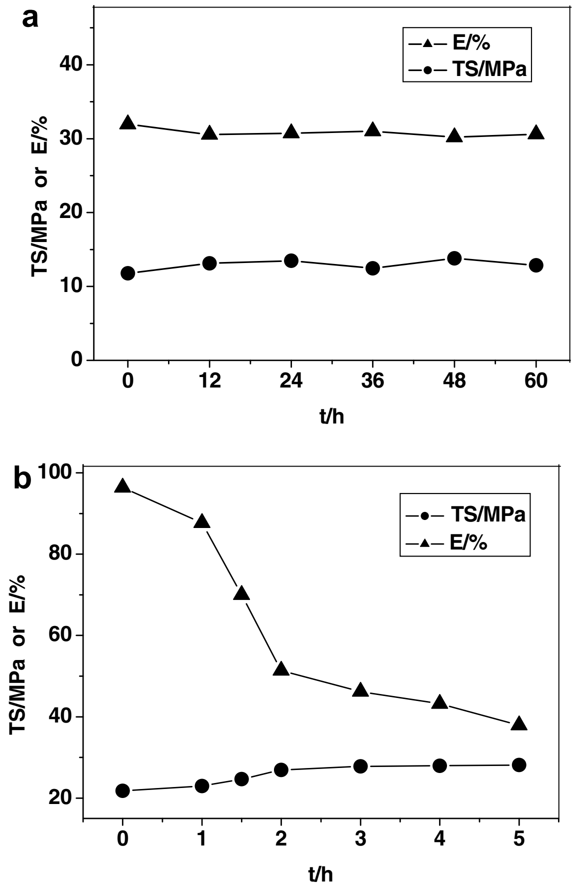

Fig. 8. Tensile strength and percent elongation at break of films in saturated formaldehyde vapor: (a) OPS films, (b) gelatin films.

film. So if the thickness of OPS film was reduced to that of PE film, the film could show high transparence and transmittance.

4. Conclusion

OPS starch films were fabricated from oxidized potato starch formulated with glycerol as plasticizer by casting method, during which the granular and crystal structure of starch was mostly destroyed by heat and shear stress under the help of glycerol, so flexible films were formed. By selecting oxidizing degree of the oxidized potato starch and adjusting the content of glycerol to control the re-crystallization and mechanical properties, we got uniform, flexible and transparent films. The OPS film with 19.4% glycerol exhibited the optimal mechanical properties similar to that of corn zein edible film, and could be satisfied with the demand of packagings. Meanwhile, the OPS films had satisfied transparence, anti-permeate for oil, and stability in acid solution, which implied that the film could be used to enclose the non-alkali oily articles. The OPS films had excellent anti-crosslinking ability for formaldehyde molecules from the air as compared with protein films like gelatin films. Moreover, the OPS film just showed slight trend of re-crystallization, which would deteriorate the flexibility of starch films, under normal temperature and humidity condition. So the OPS films had sufficient storage stability as a packaging material, especially used to enclose oily food.

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