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Effects of extrusion and glycerol content on properties of oxidized and acetylated corn starch-based films

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ABSTRACT

Oxidized and acetylated corn starch-based films were prepared by casting with glycerol as a plasticizer. The present study investigated the effects of extrusion prior to film-making and glycerol content on the properties of starch films. The films with extrusion exhibited lower tensile strength, higher elongation at break, higher water vapor permeability and higher oil permeability than those without extrusion. Extrusion reduced heat sealability of the films. With the increase of glycerol content, the films became more flexible with higher elongation at break and lower tensile strength. Water vapor permeability, oil permeability and the range between the onset temperature and the melt peak temperature rose as glycerol content increased. The thermograms indicated that plasticizers and biopolymers were compatible. These results suggested that extrusion did no good to starch films while glycerol content had apparent effect on the mechanical and barrier properties of the films.

1. Introduction

Due to the severe environmental pollution caused by plastic food packaging, there has been more and more concern on edible and biodegradable films. Starch was the most important natural polymer used to make biodegradable films because it can form a continuous matrix as a renewable and abundant resource (Bertuzzi, Armada, & Gottifredi, 2007; Lourdin, Valle, & Colonna, 1995; Romero-Bastida et al., 2005; Talja, Helen, Roos, & Jouppila, 2007). Starch-based films exhibited appropriate physical characteristics since these films were odourless, tasteless, colorless and impermeable to oxygen. However, starch exhibited several disadvantages such as a strong hydrophilic character (water sensitivity) and poor mechanical properties compared to conventional synthetic polymers (Averous & Boquillon, 2004), which severely limited their applications such as for packaging purposes. In order to overcome these drawbacks, modified starch was used to make films. Furthermore, the films made from only one kind of film-forming polymer displayed good properties in some aspects but poor properties in others. Therefore, another strategy was adopted, that is, to improve the properties of starch films by blending other biopolymers with desirable or complementary properties.

Pullulan was an excellent film-former. The regular alternation of a-(1 → 4) and a-(1 → 6) bonds resulted in distinctive structural flexibility and enhanced water-solubility (Leathers, 1993). Pullulan could produce a colorless, tasteless, odourless, transparent and flexible film that was highly impermeable to oil and heat-sealable with good oxygen barrier properties (Conca & Yang, 1993; Yuen, 1974). Despite the many potential applications of pullulan, the high cost limited its application. In this study we blended it with starch to reduce the cost and to avoid the shortcomings of starch-based films.

The addition of plasticizer was necessary to improve film flexibility. It reduced intermolecular forces and increased the mobility of polymer chains. Glycerol, as a plasticizer, had been incorporated into most hydrophilic films. It was a high boiling point plasticizer which is water-soluble, polar, nonvolatile, and starch miscible. These properties made glycerol a suitable plasticizer with a compatible water-soluble polymer (Banker, 1966). The content of glycerol affected film properties such as water sorption, WVP, mechanical properties and glass transition temperature.

The properties of films were affected by many factors including processing technology. To the best of our knowledge, few literatures reported the comparison of the films with extrusion prior to film-forming and films without extrusion. The objectives of the study, therefore, were to prepare films by blending starch and pullulan by a solution casting method, and to investigate the effect of pre-extrusion and glycerol content on the mechanical properties, barrier and thermal properties of oxidized and acetylated corn starch-based films.

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2. Experimental

2.1. Materials

Oxidized and acetylated corn starch, provided by Zhucheng Xingmao Corn Development Co., Ltd. (Weifang, China) was used to prepare starch films. Glycerol (Gly) was purchased from Chemical Reagent Co., Ltd. (Tianjin, China) and used as a plasticizer. Pullulan (PUL) was obtained from Sanqing Biological Technology Co., Ltd. (Jinan, China).

2.2. Preparation of starch–pullulan composites

Mixtures of starch, glycerol (25%, 30%, 35%, 40%, 45%, 50% of starch), pullulan (5% of starch), stearic acid (1% of starch) and glyceryl monostearate (0.5% of starch) were thoroughly blended in a SHR50A mixer (Hongji Co., Ltd., Zhangjiagang, China) at room temperature for 30 min. Blended mixtures were stored in polyethylene bags at room temperature overnight to equilibrate all components. Extrusions of the blends were done in a laboratory-scale twin screw extruder (Jingrui Plastic Machinery Co., Ltd., Laiwu, China). Temperatures of extrusion were 95 and 125 °C in I and II zone of the barrel, respectively. The mixtures were extruded at a screw speed of 30 rpm. The extrudates were ground for further use.

2.3. Film casting

The specimen powders were weighed and dispersed into distilled water (8 g/100 ml) to make film forming suspension. Film forming suspension was heated in water bath at 80 °C for 30 min by continuously mixing with an electric stirrer (Jintan Zhongda Instrument Plant, Jiangsu, China) at 300 rpm. The obtained solutions were degassed in a vacuum desiccator. Film forming suspension was poured on teflon-coated glass plates. Starch-based films were obtained by evaporating water in an oven at 50 °C for at least 5 h. The blended mixtures without extrusion were also used to make films for comparison.

2.4. Mechanical properties

Mechanical properties of the films were determined from tension tests, using the TA-XT2i texture analyzer (Stable Micro System, UK), according to ASTM D882-02 (ASTM, 2002) with some modifications. All of the tested film sheets, equilibrated at 23 ± 2 °C and 53% relative humidity ($Mg(NO_3)_2$ saturated solution) for at least 48 h prior to testing, were cut into strips (15 mm × 80 mm) with a sharp knife. The initial distance between the grips was 50 mm. The test speed was 1 mm/s. All measurements were replicated six times. The tensile strength (TS, MPa) and elongation at break (E, %) were calculated with the following equations (Tang, Alavi, & Herald, 2008):

$$\mathrm{TS} = \frac{L_p}{a} \times 10^{-6}\ \mathrm{MPa} \tag{1}$$

In this equation, L_p was the peak load (N), and a was the cross-sectional area of samples (m^2).

$$E = \frac{\Delta L}{L} \times 100 \tag{2}$$

In this equation, ΔL was the increase in length at breaking point (mm), and L was the original length (mm).

2.5. Water vapor permeability (WVP)

Water vapor permeability of the films was measured according to GB1037 with a PERME^{TM} W3/030 Automatic Water vapor permeability Tester (Languang Co., Ltd., Jinan, China). Film specimens were conditioned for 48 h in a desiccator at 23 ± 2 °C and 53% relative humidity ($Mg(NO_3)_2$ saturated solution) before analysis. The testing area of each film was 33.00 cm^2. The test temperature and relative humidity were 38 °C and 90%, respectively. The thickness of films was measured five times with a digital micrometer caliper (0–25 mm, 0.001 mm, Guanglu Digital Measurement and Control Co., Ltd., Guilin, China). Water vapor permeability of each sample was averaged from three separate tests.

2.6. Oil permeability

Salad oil of 5 ml was put into a test tube and then sealed with the specimen films. The tube was turned upside down on the filter paper and put into desiccator for two days. Oil permeability was calculated with the weight variation of filter paper, thickness, effective contact area and storage period according to the equation:

$$\mathrm{Po} = \frac{\Delta W \times \mathrm{FT}}{A \times T} \tag{3}$$

In this equation, ΔW was the weight variation of filter paper (g), FT was film thickness (mm), A was effective contact area (m^2), and T was storage period (days).

2.7. Light transmission and transparency

The visible light barrier properties of the films were measured at selected wavelengths (400–800 nm), using a UV Spectrophotometer (model UV-2100, Pgeneral Instrument Co., Ltd., Beijing, China). The starch films were cut into 4 cm × 1 cm before test. Transparency of the films was calculated as in the following equation (Han & Floros, 1997):

$$\mathrm{Transparency} = \frac{A_{600}}{X} \tag{4}$$

In this equation, A_{600} was the absorbance at 600 nm and X was film thickness (mm).

2.8. Differential scanning calorimetry (DSC)

The DSC measurements were carried out with a DSC 200PC (NETZSCH Scientific Instruments, Germany). Calibration was based on pure indium, bismuth, stannum and zinc. Samples for DSC measurements were prepared from several circular pieces cut from the polymer film to a mass of about 5 mg. Samples were scanned at a rate of 10 °C/min between temperature ranges of 50–250 °C. The DSC cell was flushed with nitrogen at a flow rate of 20 ml/min to maintain an inert environment. An empty, hermetically sealed aluminium pan was used as the reference. The transition temperatures (T_O and T_P) were determined from the thermograms obtained from the samples according to Standard ASTM D-3418 (ASTM, 2005).

2.9. Statistical analysis

Statistical differences in the film functional properties between samples were analyzed with an analysis of variance (ANOVA). Duncan's multiple range test ($p < 0.05$) was used to detect differences among mean values of film properties. Statistical analysis was conducted with SPSS 17.0.

3. Results and discussion

3.1. Film formation

A number of literatures reported that films containing glycerol under 30% were made successfully. The oxidized potato starch film

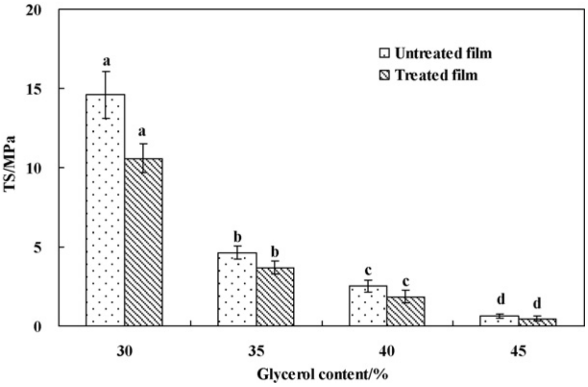

Fig. 1. Effects of extrusion and glycerol content on tensile strength (TS) of films.

with 19.4% glycerol exhibited the optimal mechanical properties similar to those of corn zein edible film, and could meet the demand of packaging (Hu, Chen, & Gao, 2009). However, films containing 25% glycerol in this study were so fragile to handle and test that no films were obtained. All the films looked clear and smooth with a smoother undersurface that was in contact with the casting surface and a rougher upper surface. It could be observed that when there is more glycerol content, thicker and more flexible films can be obtained, which could be attributed to the plasticization and concentration of glycerol. The films were sticky when the glycerol content was above 40%. The films with extrusion prior to film-forming were called treated films and the comparison ones were called untreated films in this study. The treated films were more transparent than the untreated films.

3.2. Mechanical properties

The mechanical properties of the untreated and treated films were shown in Figs. 1 and 2. The results indicated that the high temperature and strong shear treatment in extrusion process affected the mechanical properties of starch films. Tensile strength of the treated films was lower than that of the untreated films at all level of glycerol content (Fig. 1). For the films with 30% glycerol, the value of the treated film decreased about 38.1% in comparison with the untreated film. The differences of tensile strength between treated and untreated samples were not obvious which were made from 35%, 40% and 45% glycerol content. The structure of extrudates was sturdy and the number of hydrogen bonds between starch–glycerol and starch–starch increased after pre-extrusion, but some were destroyed after milling. Therefore, the tensile strength of the treated films was decreased instead of being enhanced. Another possible reason was that the extrusion process was a high temperature and strong shear procedure which promoted the plasticizing efficiency of glycerol. The force between the starch molecules was weakened and the rigid structure of the films was damaged more effectively than the untreated films. Elongation at break of the treated films was higher than that of the untreated ones and the differences were significant (Fig. 2). The elongation at break of treated film was greater than 100% when the content of glycerol was 45%. The results may also be caused by extrusion process which improved the efficiency of plasticization of glycerol with increased flexibility and receded stiffness of the films.

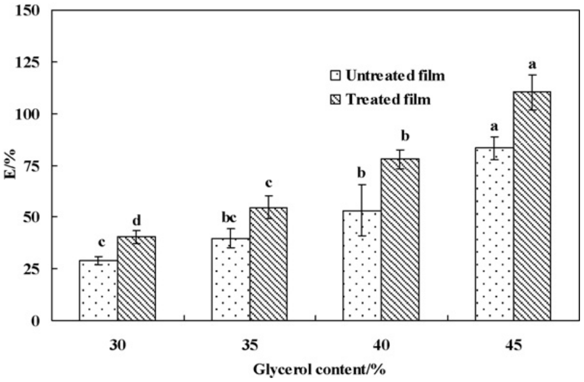

Fig. 2. Effects of extrusion and glycerol content on elongation at break (*E*) of films.

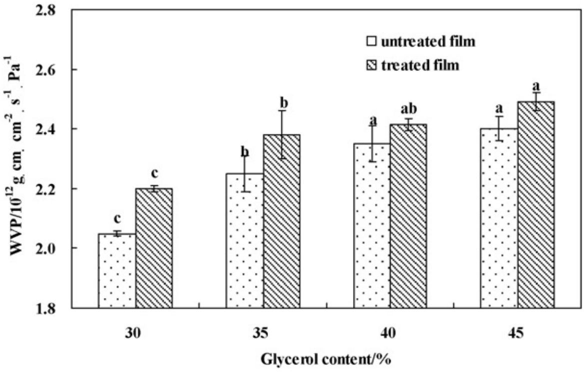

Fig. 3. Effects of extrusion and glycerol content on water vapor permeability (WVP) of films.

Tensile strength and elongation at break were markedly affected ($p < 0.0001$) by starch, moisture, glycerol, and stearic acid contents (Pushpadass, Marx, Wehling, & Hanna, 2009). As was shown in Figs. 1 and 2, values of tensile strength decreased and concurrently increased for elongation at break with increased glycerol content for the two types of films tested. The results were in agreement with most previous reports. The effect of glycerol content on the tensile strength of the two films was similar. With regard to tensile strength, it was obviously affected ($p < 0.05$) by glycerol content. The TS of the untreated films declined significantly from 14.6 to 4.7 MPa and the treated films from 10.6 to 3.7 MPa with the content of glycerol increased from 30% to 35%. Lourdin, Bizot, and Colonna (1997) observed the maximum strength of starch film plasticized with 24% glycerol as 3.0 MPa. Colla, Sobral, and Menegalli (2006) studied the effects of stearic acid and glycerol on amaranthus flour films, and reported tensile strength and elongation at break values of 2.6 MPa and 148%, respectively. The addition of pullulan may result in higher values of tensile strength in the present study.

The elongation at break of the films increased steadily with the increase of glycerol content, ranging from 28.8% to 83.3% for the untreated and 40.3% to 110.3% for the treated films, respectively. The results corresponded with the typical mechanical behavior of ductile polymer–plasticizer systems, in which the elongation at break is expected to increase with an increase in glycerol or other plasticizers content (Lourdin et al., 1997; Shogren, 1992).

The effect of glycerol content on starch films can be explained by plasticizing theory. The reduction of intermolecular interactions and the cohesion between the starch chains by the plasticizers were called blocking effect (Turhan & Sahbaz, 2004). Usually, plasticizers accomplished the blocking effect by interfering with direct intermolecular interactions and an increase of free volume between the starch polymers (Mali, Grossmann, Garcia, Martino, & Zaritzky, 2002; Turhan & Sahbaz, 2004).

3.3. Water vapor permeability (WVP)

The WVP of treated films was higher than that of the untreated films (Fig. 3). Extrusion may have resulted in a certain degree of depolymerization and the breaking of hydrogen

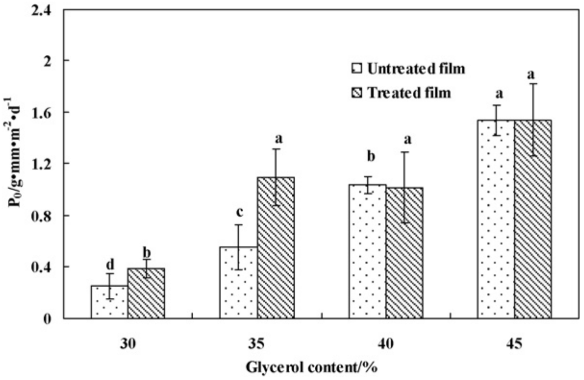

Fig. 4. Effects of extrusion and glycerol content on the oil permeability of films.

bonds in starch, which in turn facilitated absorption of water. The values of WVP ranged from 2.05×10^{-12} to 2.40×10^{-12} g cm cm^{-2} s^{-1} Pa^{-1} for the treated films and from 2.20×10^{-12} to 2.49×10^{-12} g cm cm^{-2} s^{-1} Pa^{-1} for the untreated films (Fig. 3). All the films tested in this study had higher WVP than low density polyethylene (LPDE) (0.036×10^{-10} g m^{-1} Pa^{-1}) (Shellhammer & Krochta, 1997). A reasonable assumption for the higher values for WVP was that the films held substantial amount of water within the starch–plasticizer network. The absorbed moisture, due to plasticization, had a swelling effect that tended to increase the film permeability to water vapor. Swelling also disrupted the structural integrity and barrier properties of the polymer network (Pushpadass et al., 2009).

The increase of WVP with increased glycerol concentration may be caused by the structural modifications in the starch network and the hydrophilicity and water holding capacity of glycerol, which served as a minimum barrier to the movement of moisture and facilitated the absorption and diffusion of water molecules (Bertuzzi, Vidaurre, Armada, & Gottifredi, 2007).

Some studies showed that the increase in film thickness could also result in an increase of WVP value. According to Cuq, Gontard, Cuq, and Guilbert (1996), thickness was a significant variable when barrier properties are taken into account. McHugh, Avena-Bustillos, and Krochta (1993) attributed the thickness effects to relative humidity. They observed that resistance of the films to water vapor reduced as the thickness increased. As a result, a stagnant air layer formed, characterized by a partial pressure of high water vapor on the inner film surface.

Table 2
The effect of extrusion and glycerol content on thermal properties of the films.

Type of films	Content of glycerol (%)	T_O (°C)	T_P (°C)	Range ($T_P - T_O$) (°C)
Untreated	30	172.3	198.8	26.5
	35	153.4	182.0	28.6
	40	151.9	183.4	31.5
	45	150.5	186.0	35.5
Treated	30	132.7	159.4	26.7
	35	170.3	206.9	36.6
	40	164.5	225.9	61.4
	45	141.4	221.7	80.3

3.4. Oil permeability

The oil permeability of films was showed in Fig. 4. The treated films had higher oil permeability. It was assumed that extrusion promoted the plasticization and that glycerol increased free volume between the starch polymers which made oil permeate easily. The values of P_o increased with the increase of glycerol content, which was contrary to previous reports (Zhou & Zhang, 2006). Although glycerol contained hydrophilic hydroxyl which could restrain oil transmission through the films, the impact could not counteract with plasticization.

3.5. Light transmission and transparency

The light transmission rates for all starch-based films were higher than 82% (Table 1) which indicated that the components of the films were well compatible and the films made in this study were colorless and clean. Most light transmission rates of the films were higher than those of the synthetic films displayed in Table 1. The values of the treated films were higher than those of the untreated films which suggested that extrusion made the compositions more compatible with high shear force and high temperature. With constant wavelength, the films containing 35% glycerol had the highest light transmission rate and the ones containing 30% glycerol had the lowest.

The light transmission rate in the visible region (400–800 nm) increased as wavelength increased for all samples. The wavelength of 600 nm is commonly used for the film transparency measurement (Fang, Tung, Britt, Yada, & Dalgleish, 2002; Han & Floros, 1997; Shiku, Hamaguchi, & Tanaka, 2003). So it was selected to determine the transparency of films in this research. With the increase of glycerol content, the transparency values gradually decreased. The transparency values of the films in this research were lower

Table 1
The effect of extrusion and glycerol content on light transmission and transparency of films.

Film type	Glycerol content (%)	Wavelength (nm)					Transparency
		400	500	600	700	800	
		Light transmission[a]					
Untreated	30	85.5 ± 0.86a	86.7 ± 0.92a	87.5 ± 0.81a	88.1 ± 0.73a	88.3 ± 0.73a	1.08 ± 0.27
	35	87.5 ± 0.73a	88.7 ± 0.51a	89.2 ± 0.52c	89.6 ± 0.32c	89.6 ± 0.12a	1.05 ± 0.08
	40	87.0 ± 0.61a	88.2 ± 0.51a	88.9 ± 0.52bc	89.3 ± 0.52bc	89.4 ± 0.43a	0.65 ± 0.12
	45	86.5 ± 2.06a	87.7 ± 1.85a	88.2 ± 1.46ab	88.7 ± 1.42ab	89.1 ± 1.39a	0.46 ± 0.06
Treated	30	82.8 ± 0.2a	85.9 ± 0a	87.1 ± 0a	87.1 ± 0a	88.1 ± 0a	0.71 ± 0.022
	35	87.3 ± 0.53b	89.54 ± 0.36c	90.4 ± 0.43c	90.8 ± 0.36c	91.0 ± 0.36c	0.70 ± 0.022
	40	87.0 ± 0.31b	88.8 ± 0.24b	89.5 ± 0.21b	90.0 ± 0.12b	90.2 ± 0b	0.66 ± 0.011
	45	87.0 ± 0.12b	88.8 ± 0.31b	89.5 ± 0.31b	89.9 ± 0.52b	90.0 ± 0.41b	0.62 ± 0.022
LDPE[b]	–	83.4	85.6	86.9	87.8	83.6	3.05
OPP[b]	–	87.9	88.8	89	89.3	89.6	1.67
PE[b]	–	73.6	82.1	83.5	84.2	84.9	1.51
PVDC[b]	–	86.6	87.5	90.0	87.9	84.9	4.58

[a] Different lowercase letters in the same row under the same wavelength and treatment indicated significant differences ($p < 0.05$). Data shown in mean ± standard deviation ($n = 3$).

[b] From Shiku et al. (2003), LDPE: low-density polyethylene; OPP: oriented polypropylene; PE: polyester; PVDC: polyvinylidene chloride.

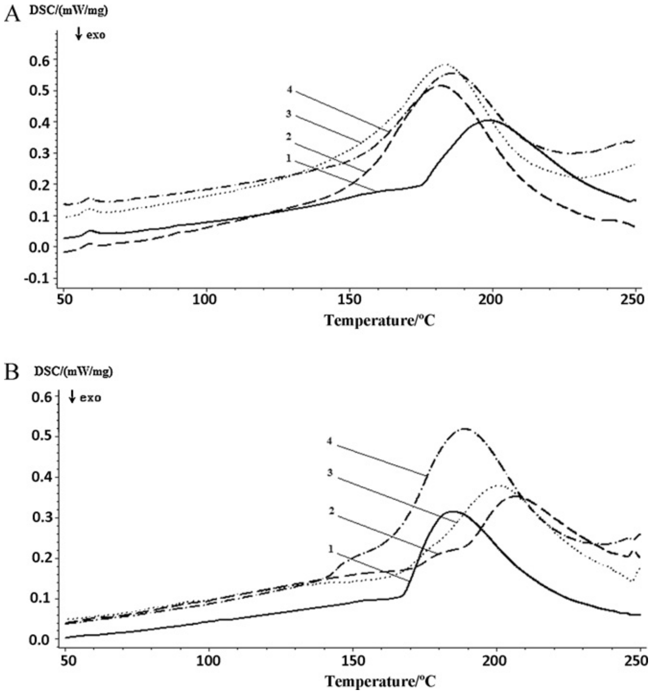

Fig. 5. (A) Differential scanning calorimetry thermograms of films without extrusion (glycerol content: 1, 30% glycerol; 2, 35% glycerol; 3, 40% glycerol; 4, 45% glycerol). (B) Differential scanning calorimetry thermograms of films with extrusion (glycerol content: 1, 30% glycerol; 2, 35% glycerol; 3, 40% glycerol; 4, 45% glycerol).

than those of the synthetic films because of the high light transmission rates. The results indicated that oxidized and acetylated corn starch-based films were clear enough to be used as transparent inner-food packaging material.

3.6. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a common method for the determination of transition temperatures. Thermal transition temperatures are typically used to determine sealing temperatures of polymers (Hernandez, 1997). Table 2 showed the peak and onset temperatures for all specimen films. The range between the peak temperature and the onset temperature of the treated films were broader than that of the untreated films. If the T_{O} and T_{P} values were very close, the film would mostly melt when it is used in sealing. At this temperature, the film lost its structure (Tanner et al., 2003). So we could conclude that extrusion process had a negative effect on the heat sealability of starch films.

For the untreated films, the onset temperature decreased with the increase of glycerol content. The trend also could be seen in the treated films except in the film containing 30% glycerol. The increase of glycerol content resulted in the T_{O} closer to the common heat-sealing temperature, which improved the sealing process. The range between T_{P} and T_{O} of all the films was broader with the increase of glycerol content. The effects of glycerol on thermal properties were very complicated due to the interaction between water and other plasticizers in plasticization (Abdorreza, Cheng, & Karim, 2011).

The starch–starch and starch–plasticizer interactions could also be investigated by the differential scanning calorimetry (DSC). Melting peak and flow area were observable in the starch-based films because starch was thermoplastic biopolymer (Fig. 5). Starch–pullulan complex films exhibited single sharp transition peak that shifted with different content of glycerol. In the case of immiscible blends such as poly (hydroxybutyrate-cohydroxyvalerate) and poly (ε-caprolactone), two distinct melting temperatures have been reported (Chun & Kim, 2000). Thermograms suggested that plasticizer and biopolymers remained a homogeneous material throughout the temperature range, because phase separation between plasticizer and biopolymers was not observed.

In Fig. 5(A), a small peak at approximate 58 °C was found in the untreated film with varied glycerol content. However, the peak was not seen in the treated film in Fig. 5(B). The small peak was regarded as the crystal melting peak of the remaining crystallites of starch. The untreated films were not completely gelatinized and remained partially starch granules, therefore, the crystal melting peak appeared, while the treated films underwent the high temperature and strong shear force which promoted gelatinization. So we did not find the crystal melting peak of the treated film.

In Fig. 5(B), when glycerol content was more than 35%, the DSC peak was seperated into two peaks. There was a secondary peak on the left of main peak. The slight melting endotherm denoted the melting of amylose–lipid complexes formed by extrusion. This conclusion was testified by the absence of such melting endotherms in the DSC profiles of films without extrusion in Fig. 5(A). It was assumed that extrusion of starch-based powder at high temperature resulted in formation of complexes between amylose and lipids. Pushpadass, Marx, and Hanna (2008) reported temperature range of 112.5–133.0 °C was assigned to the melting of amylose–lipid complexes formed by extrusion.

4. Conclusion

Effects of extrusion and glycerol content on the mechanical properties, water vapor permeability, oil permeability, transparency, and heat sealability of the oxidized and acetylated corn starch-based films were investigated. Extrusion prior to film-making could enhance the elongation at break, and reduce the barrier properties. Water vapor permeability and oil permeability of the films with extrusion were higher than those of the untreated films. The transparency of treated films was lower than that of the untreated. The rang between peak temperature and the onset temperature of the treated films were broader than the untreated films which indicated that the pre-extrusion had negative effect on the heat sealability of films. The treated films were completely gelatinized because of pre-extrusion. The content of glycerol had significant effect on the properties of films. Increased glycerol content reduced tensile strength of the films and barrier properties. High glycerol content was adverse to heat sealability. Thermograms indicated that plasticizers and biopolymers were compatible.

In short, oxidized and acetylated corn starch could be used to make biodegradable films with good properties. The properties of the treated films exhibited the same variation trend with the increase of glycerol content as the untreated films. Glycerol content had significant effect on the properties of films and should be considered in the formation of films.

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