

Characterization of Extruded Film Based on Thermoplastic Potato Flour

Yachuan Zhang,^{1*} Xin Yuan,² Michael R. Thompson,² Qiang Liu¹

¹Guelph Food Research Centre, Agriculture and Agri-Food Canada, Guelph, Ontario N1G 5C9, Canada

²Department of Chemical Engineering, McMaster University, Hamilton, Ontario L8S 4L8, Canada

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ABSTRACT: Potato flour is abundant and less expensive than starch, though its major component is starch. It would therefore seem to be an attractive and viable source of biomass for biodegradable thermoplastic products. This study prepared thermoplastic potato flour (TPF) and thermoplastic potato starch (TPS) films by extrusion and investigated their properties. A mixture of glycerol and triethyl citrate (25–35% of total weight) was chosen for the plasticizer. Properties of the TPF film, such as mechanical properties, surface hydrophilicity, surface energy, moisture sorption isotherm, and glass transition temperature (T_g), were characterized and compared with TPS film. The results showed that TPF film was comparable to TPS film in many properties. The mechanical properties of the TPF

film, including tensile strength, elongation at break, and tensile modulus, were similar in magnitude to TPS film. In addition, TPF film showed lower T_g and surface hydrophilicity, but higher surface wetting capacity than TPS film. Components other than starch in potato flour were believed to have had a plasticization effect on TPF properties. Overall, potato flour demonstrated a comparable capacity for manufacturing thermoplastic film similar to the more expensive starch feedstock. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 3250–3258, 2012

Key words: potato flour; film; surface tension; hydrophilicity; moisture sorption isotherm

INTRODUCTION

Starch is considered as one of several promising raw materials for the production of biodegradable plastics.¹ Much effort has been made to develop starch-based thermoplastics,^{2,3} and considerable progress has been achieved. Besides starch, the use of flour in bioplastic production, such as potato flour, wheat flour, or rice flour, is expected to yield products with properties similar to those of existing starch-based thermoplastics. Potato flour is usually composed of more than 65% starch, with the remaining being mostly protein and fiber. As a raw material for bioplastic production, potato flour is stable, versatile, inexpensive, and available throughout the year. In addition, the use of potato flour also can potentially reduce the production cost of bioplastics since fewer purification steps are needed from raw potato compared to starch. Conventionally, potato

flour is used as a thickener in soup, gravy, fabricated snacks, and bakery products. No prior application of potato flour in thermoplastics has been reported in literature.

In this study, potato flour was used to prepare thermoplastic flour (TPF) by extrusion. In contrast with conventional thermoplastic starch (TPS), properties of TPF can be influenced by not only the starch component, but also the protein and fiber components in potato flour. The objective of this study was to prepare TPF film and characterize its physical and mechanical properties. Properties, such as tensile properties, thermo-mechanical properties, moisture sorption isotherm, surface energy, and surface hydrophilicity, etc. were determined and compared with those of its counterpart—the TPS film.

MATERIALS AND METHODS

Materials

The potato source was a Norland variety grown under organic conditions in Prince Edward Island, Canada, in 2007. Potato starch was extracted from raw organic Norland potato. Potato flour was obtained from the same source following the method of Liu et al.⁴ The potato flour contains $70.3 \pm 0.3\%$ starch (dry basis), $13.1 \pm 0.3\%$ protein (d.b), and $30.8 \pm 0.3\%$ apparent amylose (d.b). The moisture

*Present address: Richardson Centre for Functional Foods and Nutraceuticals, University of Manitoba, Winnipeg, MB, R3T 2N2, Canada.

Correspondence to: Q. Liu (Qiang.Liu@AGR.GC.CA).

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TABLE I
Formulation of Film Compound (w/w, %)

Sample	Flour	Starch	Glycerol	Triethyl Citrate
F1	75	0	22.5	2.5
F2	70	0	27	3
F3	65	0	31.5	3.5
S1	0	75	22.5	2.5
S2	0	70	27	3
S3	0	65	31.5	3.5

content of flour was analyzed in the laboratory before extrusion, which was $\sim 9.22\%$ (wet basis). Potato starch contains 7.7–8.9% moisture content. Detailed information on the preparation and analysis data of starch and flour can be found in the report of Donner et al.⁵ Glycerol and triethyl citrate were purchased from Sigma-Aldrich (St. Louis, MO), and SAFC Supply Solutions (St. Louis, MO), respectively, acting as plasticizers.

Preparation of TPF and TPS films

The ingredient formulations used to prepare TPF and TPS were listed in Table I. Flour and starch were each mixed with plasticizers at three weight compositions: 25, 30, and 35% of plasticizers with the remaining as flour or starch. A mix of two plasticizers was used: glycerol and triethyl citrate. The weight ratio between glycerol and triethyl citrate was kept as a constant of 9 : 1 for all samples. Triethyl citrate also acted as a glidant which aided feeding of the powders into the extruder. All components were manually mixed in sealed plastic bags, and then stored under room temperature (23°C) for more than 24 h before being processed.

The mixed samples were processed by a twin-screw extruder (Micro 15 mL Screw Compounder, Model 2005, DSM Xplore, Geleen, Netherlands). A constant temperature of 125°C was controlled collectively in feed, metering, compression, and die sections. Each blend was processed in the extruder for 12 min in recycling mode at a screw speed of 100 rpm. When the films were subsequently being extruded, the screw speed was reduced to 15 rpm. A ribbon die with 35 mm width and 0.4-mm gap was used to produce the films. The films were collected on a torque winder (DSM Film Device, Xplore, Geleen, Netherlands), which was set at a peripheral speed of 150 mm/min and torque of 19 N·mm. The films were cut into around 15 cm lengths and conditioned in a desiccator having a relative humidity (RH) of $52 \pm 1\%$ at $22 \pm 1^\circ\text{C}$ for up to 10 days. The humidity level was achieved with a saturated $\text{Mg}(\text{NO}_3)_2$ solution, above which the film specimens were placed. Because of insufficient plas-

ticization effect, no film could be made from the S1 formulation, which contained 25% plasticizer.

Tensile property measurements

Film specimens were cut into rectangular strips, 1 cm wide and 8 cm long, then conditioned in $52 \pm 1\%$ relative humidity for 10 days using a saturated solution of $\text{Mg}(\text{NO}_3)_2$ at $22 \pm 1^\circ\text{C}$. Film thickness was measured using an electronic digital micrometer (Mitutoyo, Japan; 0.001-mm sensitivity) at three random positions on each film, which was in the range of 0.27–0.34 mm. A Universal Test System (Series 701 system, Com-Ten Industries, Pinellas Park, FL) was used to determine the apparent values of ultimate tensile strength (TS) and elongation-at-break (E) following the procedure of Zhang et al.,^{6,7} which is a modified method from ASTM method D882-91.⁸ The ends of the cut films were clamped with grips, and then stretched using a crosshead speed of 10 mm/min. The mechanical properties were determined in room condition of $22 \pm 1^\circ\text{C}$ and $52 \pm 1\%$ RH. Data of TS, E, and TM were obtained from five replicates.

Critical surface energy of wetting

Critical surface free energy (γ_c) of the film was measured using the Zisman method, which measures variation in contact angle (θ) as a function of the known surface tension, γ_l , for a series of liquids. The procedure followed Han et al.⁹ with some minor modifications. Three probe liquids, glycerol (Sigma-Aldrich, St. Louis, MO), thiodiglycol (2, 2'-thiobisethanol) (Sigma-Aldrich, St. Louis, MO), and ethylene glycol (Fisher Scientific, Fair Lawn, NJ) were chosen to measure θ , which have γ_l of 0.064, 0.054, and 0.0477 N/m respectively. Water was not used in the θ measurement as preliminary tests showed that water was absorbed quickly into the films due to the high hydrophilicity of the starch and flour. A computer controlled goniometer system (EasyDrop standard Drop Shape Analysis System, KRÜSS GmbH, Hamburg, Germany) was used. Each film specimen was spread evenly on a rigid flat surface, which was mounted onto the sample stand of the goniometer. A drop of 3 μL liquid was deposited on the film sample with a micro syringe. The contact angles on both sides of the drop were collected. For each liquid, at least ten measurements at different positions of the film were made. All the experiments were done in the room condition of $22 \pm 1^\circ\text{C}$ and $52 \pm 1\%$ RH. A Fox-Zisman plot for each film was created by plotting the $\cos\theta$ values against their respective γ_l . γ_c was then estimated by extrapolating the best fit line obtained from the linear regression of $\cos\theta$ against γ_l to $\cos\theta$ equal to 1. Nine measurements were performed for each film.

Surface hydrophilicity

The water contact angle (θ) on film samples was measured using the sessile drop technique with a goniometer (EasyDrop standard Drop Shape Analysis System, KRUSS GmbH, Hamburg, Germany). Totally 3 μ L of distilled water was placed by a software-controlled syringe on a small piece of film for each measurement. The water θ was measured on both sides of the water drop at 3-s interval for 15 s after water drop was deposited onto the film sample and averaged automatically by Drop Shape Analysis software for flour films. For starch films, the measurement was taken at 0.5-s interval for 3 s. A minimum of three measurements at different positions on the film was carried out. All contact angle measurements were performed at ambient condition of $22 \pm 1^\circ\text{C}$ and $52 \pm 1\%$ RH. Water absorption rate was assumed related to the rate of contact angle change, which was represented by the slope of water θ against time. In order to calculate the slope accurately, linear regression of water θ against time was performed on multiple repeated measurements. Only results with coefficient of correlation (R^2) higher than 0.8 were accepted. Triplicate accepted results were obtained for each sample film to assess the measurement error. Because no S1 film was available, water θ was measured only on the other five flour and starch samples.

Moisture content

The moisture contents of processed films were determined by first weighing about 0.8 g sample in an aluminum pan. Then the samples were dried in a forced air oven (Model 750F, Isotemp Standard and Premium Ovens, 700 Series, Fisher Scientific) for 24 h at 105°C . After the samples were completely dried, they were cooled and reweighed. The moisture content (MC, wet basis) of each sample can then be calculated by eq. (1),

$$\text{MC} = \frac{W_o - W_d}{W_o} \times 100\% \quad (1)$$

where W_o is the weight of original sample, and W_d is the weight of dried sample. Triplicate measurements were performed for each formulation of flour and starch type films.

Water solubility index

Film samples were cut into small pieces and dried in a forced air oven at 105°C for 24 h. The completely dried film pieces were weighed as W_d , and then put in a capped 50 mL plastic test tube with 25 mL of distilled water. The tubes were subjected to

occasional manual shaking and stored at room condition for 24 h. The residual undissolved film was removed carefully using a lab spatula from the tube and put into an aluminum pan for drying in the forced air oven at 105°C for 24 h again. After drying, the dried undissolved film was weighed and as W_f . The water solubility index (WSI) of the film was calculated according to the eq. (2).

$$\text{WSI} = \frac{W_d - W_f}{W_d} \times 100\% \quad (2)$$

where W_d is the initial dry weight of the film, and W_f is the weight of the dried undissolved film. Triplicate measurements were obtained for each sample.

Moisture sorption isotherm

Water sorption properties of various films were determined by first conditioning the samples in sealed desiccators under eight different RH levels. The constant RH in desiccators were controlled by different saturated salt solutions, including LiCl, CH_3COOK , MgCl_2 , K_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, NH_4NO_3 , NaCl, and KCl, which were shown to maintain RH levels of 12, 22, 33, 43, 53, 63, 75, and 85% RH, respectively.^{6,7} The film samples were placed in the preconditioned desiccators for 7 days. The equilibrium moisture content (MC, dry basis) of each sample was determined gravimetrically by exposing about 0.5 g of each sample to 105°C for 24 h in a forced air oven. The water activity (a_w) of a sample was measured with a water activity meter (Pawkit, Decagon Devices, Pullman, WA). Three replicate measurements of water activity were obtained for sample under each RH level, and the average values were used. The moisture isotherm curves were created by plotting MC against a_w . Water sorption behavior of the films was modeled with the Guggenheim-Anderson-de Bour (GAB) equation¹⁰ listed as follows.

$$M = ABCa_w / (1 - Ca_w) \times (1 - Ca_w + BCa_w) \quad (3)$$

where M is equilibrium moisture (g water /100g dry matter); a_w is water activity of the samples, A is the monolayer moisture content (water g/100 g, dry basis), B is the Guggenheim constant, which is a correction factor for the sorption properties of the 1st layer with respect to the bulk liquid, and C is a correction factor for the properties of the multilayer with respect to the bulk liquid. The parameters of the GAB model were estimated by the nonlinear regression procedure in SAS software (SAS Inst, Cary, NC). The goodness of fit for the GAB model was evaluated by the mean of the relative percent difference between the experimental data and

predicted values of the MC, which is defined as the mean relative deviation modulus (G).

$$G = (100/n) \sum_{i=1}^n \left(\frac{|M_{ai} - M_{pi}|}{M_{ai}} \right) \quad (4)$$

where n is the number of observations, M_{ai} is the experimentally determined MC of i -th data, and M_{pi} is the predicted MC of the i -th data by models. A G value lower than five indicates excellent fit of the model to actual measurements, while a G value between 5 and 10 suggests a reasonably good fit, and a G value greater than 10 is considered a poor fit.^{11–13}

Sample specific surface area, S_0 , was determined from the monolayer moisture content. Equation (5) was used to calculate S_0 .^{11,14} S_0 is an important concept in describing the surface characters and water binding properties of the samples.

$$S_0 = M_m \times \frac{N_0 \times A_{H_2O}}{M_{H_2O}} = 3.5 \times 10^3 \times M_m \quad (5)$$

where S_0 is the specific surface area ($\text{m}^2 \text{g}^{-1}$), M_m is the monolayer moisture (parameter A in GAB model divided by 100) (water g g^{-1} , db), M_{H_2O} is the molecular weight of water (18 g mol^{-1}), N_0 is Avogadro's constant ($6 \times 10^{23} \text{ molecules mol}^{-1}$), and A_{H_2O} is the area of one water molecule ($1.06 \times 10^{-19} \text{ m}^2$).

Dynamic mechanical thermal analysis

Dynamic mechanical analysis (DMA) was performed to determine the glass transition temperature (T_g) of film samples. The DMA was carried out by a Q800 Dynamic Mechanical Analyzer (TA Instruments-Water LLC, New Castle, Del., USA), which was equipped with a DMA-RH accessory and a nitrogen gas cylinder for humidity control. Film tension clamps were used in Multi-Frequency-Strain mode. Totally, 50% RH was kept constant inside sample chamber, while 1 Hz of oscillation frequency and 15 μm of amplitude were used during the measurement. Temperature sweep rate was $1^\circ\text{C}/\text{min}$ from 5°C to 100°C , which is the only choice for the DMA with RH accessory. Film sample was cut into a rectangular shape with dimensions of $\sim 32.0 \text{ mm} \times 7.0 \text{ mm} \times 0.25 \text{ mm}$ ($l \times w \times t$). For each analysis, the DMA recorded values of loss factor, $\tan \delta$ ($\tan \delta = E''/E'$, where E' is the storage modulus, and E'' the loss modulus) against temperature. The glass transition temperature (T_g) was defined as the peak of $\tan \delta$. Duplicate measurements were obtained for each sample.

Statistical analysis

A completely full randomized experimental design was used. Data were analyzed by one-way ANOVA

using SAS (SAS Institute, Cary, NC) to assess the effects of flour and plasticizer on the properties of starch films. Mean values with standard deviations were compared using a Tukey's mean difference test at 95% significance level.

RESULTS AND DISCUSSION

Extrusion process and film description

Preliminary experiments performed in our laboratories demonstrated that liquid plasticizer should be in the range of 25–35% of total weight to yield acceptable products. Higher amount of plasticizer led to exudation, while lower amount resulted in difficulty of processing in the extruder. The extruder and ribbon die worked consistently without surging or exceeding the torque limits of the machine when the plasticizer amount was around 30%. For S1 formulation containing 25% plasticizer, no satisfactory film specimens could be produced due to the extremely low fluidity of the melt inside the extruder, which could not flow through the ribbon die. Instead, only string extrudate of S1 was obtained from a strand die.

The film samples produced with flour were distinctively different in appearance from those produced with starch. The flour samples acquired a dark brown color after being extruded, while the starch samples remained light yellow or white. Both materials were opaque. In addition, the flour samples generated an unpleasant burnt smell during extrusion, while the starch samples remained relatively odorless. Moreover, both flour and starch samples were slightly sticky to the touch. The stickiness also seemed to increase slightly as the plasticizer amount in formulation increased.

Mechanical properties

Figure 1(A) shows that the TPF and TPS film samples had TS in the range of 0.8–2.6 MPa, which were in agreement with previously reported values (e.g., TS between 0.2 and 4.8 MPa).^{15–17} As expected, the TS shown in Figure 1(A) decreased progressively and proportionally with increasing concentration of plasticizer in the samples. For example, the TS decreased by 68% as the plasticizer concentration increased from 25 to 35% in the flour films. Statistical analysis shows that the F1 film displayed a similar TS value as S2 film (no significant difference at $P < 0.05$), indicating that the additional components present exclusively in flour, such as proteins and fiber, etc., contributed to structural heterogeneity in the matrix to the same order as a higher level of plasticizers in the starch films. Figure 1(B) shows elongation at break (E) of the film samples was in the range of 4–11%, which was lower than the

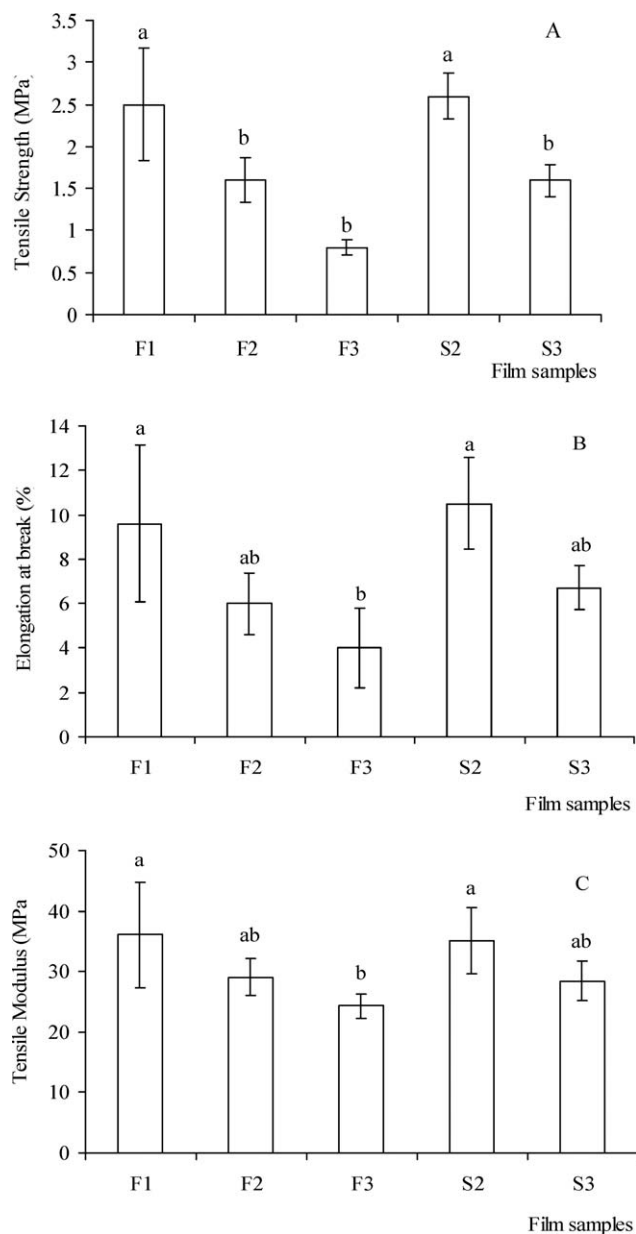


Figure 1 Tensile properties of TPF and TPS films. Means with the same letters are not significantly different ($p < 0.05$, $n = 5$).

results reported previously. Colla et al.¹⁶ observed E values of *Amaranthus cruentus* flour films from 74 to 620%. In addition, Pushpadass et al.¹⁵ observed E values of corn starch films from 44 to 91%. Figure 1(B) shows that with increasing the plasticizer content from 25 to 35%, E decreased from 10 to 4% for flour films. For starch films, even though the E was not significantly different (at $P < 0.05$), the trend of E was decreasing with higher plasticizer amount. This is in agreement with Pushpadass et al.,¹⁵ but contradictory to the general rule that more plasticizer increases E of polymers. One explanation for this phenomenon is phase-separation. When glycerol was greater than 30% (w/w), these films contained two separated phases with one being starch (or flour)-rich phase, another being plasticizer-rich phase, and led to a reduced E value.¹⁸ Figure 1(C) shows TM of TPF and TPS films ranged from 24 to 36 MPa, which were in agreement with the values reported by Pushpadass et al.,¹⁵ who observed that extruded corn starch films had TM of 3–38 MPa. Figure 1(C) shows a decreasing trend of TM with increasing plasticizer concentration. According to Zhang et al.,³ increase in plasticizer content could result in a decrease of intermolecular interactions between the starch polymers. Thus, starch polymer chains had less cohesive force and the films became more flexible, indicated by a lower TM. Overall, data shown in Figure 1 indicated that the TPF film was comparable to TPS film in TS, E , and TM. The components other than starch present in flour contributed to mechanical properties of flour film to the same order as a higher level of plasticizer in the starch film.

Critical surface energy of wetting

Table II shows probe liquid contact angles and γ_c for all sample films, indicating that TPS and TPF films had γ_c values of 0.036–0.037 and 0.042–0.046 N/m, respectively. According to Zisman theory, liquids with γ_l lower than 0.036 N/m can spread on the TPS films, and liquids with γ_l lower than 0.042 N/m can

TABLE II
Film Probe Liquid Contact Angle (θ), and Critical Surface Energy (γ_c)^a

Sample	Contact angle (θ , °)			γ_c (N/m)
	Ethylene glycol	Thiodiglycol	Glycerol	
F1	20.5 ± 3.5	34.4 ± 4.5	60.2 ± 2.9	0.046 ± 0.001 ^a
F2	25.4 ± 3.0	28.6 ± 3.6	48.4 ± 4.5	0.042 ± 0.002 ^a
F3	29.1 ± 4.1	29.4 ± 3.3	49.3 ± 5.2	0.042 ± 0.002 ^a
S1	–	–	–	–
S2	15.5 ± 4.1	24.5 ± 4.4	29.4 ± 5.3	0.037 ± 0.005 ^b
S3	16.4 ± 2.4	21.7 ± 3.9	27.2 ± 5.1	0.036 ± 0.005 ^b

^a Values are means ± standard deviation ($n = 9$). Different superscripts in the column indicate significant difference at $P < 0.05$.

TABLE III
Water Contact Angle (θ), Slope of Regression Lines of Water Contact Angle, Moisture Content (MC), Water Solubility Index (WSI), and Glass Transition Temperature (T_g) for Thermoplastic Flour (TPF) and Thermoplastic Starch (TPS) Film^a

Sample	Water contact angle (θ , °) ^b	Slope of regression lines of water contact (deg./s) ^{b, c}	MC (%) ^b	WSI (%) ^b	T_g (°C) ^d
F1	22.2 ± 5.8 ^A	-0.41 ± 0.07 ^A	11.1 ± 0.4 ^A	30.5 ± 0.2 ^A	19.5 ± 1.9 ^{A, B}
F2	18.9 ± 4.7 ^A	-0.42 ± 0.10 ^A	21.7 ± 1.4 ^C	33.4 ± 0.9 ^B	11.7 ± 1.1 ^C
F3	20.5 ± 5.5 ^A	-0.41 ± 0.09 ^A	23.2 ± 1.2 ^{C, D}	36.3 ± 0.1 ^C	4.5 ± 0.3 ^D
S1	—	—	10.0 ± 0.8 ^A	20.1 ± 0.9 ^D	—
S2	7.5 ± 3.9 ^B	-2.49 ± 0.25 ^B	14.5 ± 0.6 ^B	21.1 ± 1.3 ^{D, E}	24.7 ± 2.8 ^A
S3	8.5 ± 4.5 ^B	-2.19 ± 0.57 ^B	25.5 ± 0.7 ^D	23.7 ± 1.7 ^E	17.1 ± 0.8 ^{B, C}

^a Different superscripts in the column indicate significant difference at $p < 0.05$.

^b Values are means ± standard deviation ($n = 3$).

^c Absorption rate represented by rate of change of contact angle obtained from regression analysis.

^d Values are means ± standard deviation ($n = 2$).

spread on the TPF films successfully. The results in this study are in agreements with Gopalakrishnan et al.¹⁹ and Cyras et al.²⁰, who observed surface tension of about 0.043 N/m for wheat flour film, and 0.040 N/m for TPS/montmorillonite nanocomposite films. Table II shows that the TPF samples had higher γ_c values than TPS samples ($P < 0.05$), indicating TPF films had better wettability. The increase in γ_c of TPF samples was probably due to proteins and fibers contained in TPF which resulted in increase in the surface energy.

Surface hydrophilicity

Film surface hydrophilicity can be reflected by water contact angle (θ).²¹ Water on hydrophilic surfaces will exhibit a low contact angle. Results are displayed in Table III, and showed TPF and TPS films had 19–22° and 8–9° contact angle respectively, indicating both of them were hydrophilic (contact angle $< 45^\circ$). Statistical analysis showed TPF film had a significantly higher θ than TPS film ($P < 0.05$), indicating the TPF film surface was less hydrophilic than TPS film surface.

Figure 2 shows the change of θ against time with standard deviation as error bars. Water adsorption rate of TPS and TPF samples can be represented by the change of θ against time. The slopes of best fit lines in Figure 2 were obtained from linear regression to represent the rate of change of θ . The results were listed in Table III. The slope values were negative since water contact angle always decreased with time due to absorption. The faster the water contact angle decreased, the higher the sample's water absorption rate was, and the lower the slope of the fit line. TPS films had much lower slope values than TPF films, suggesting that the TPS film surface absorbed water faster than the TPF film surface. In fact, the θ on TPS samples had to be measured

within several seconds, since the contact angle quickly diminished to zero in only 10 s after the water droplet was deposited on the TPS film surface. Importantly, the errors displayed for TPS were large, indicating that θ results were highly variable, which was due to fast water absorption and swelling of the TPS film surface. Statistical analysis shows that all TPF films had approximately the same water absorption rate, no matter how much plasticizer they contained, and TPS films also had same water absorption rate among themselves.

Moisture content

The moisture contents (MC, wet basis) of samples conditioned under 52% RH are displayed in Table III. The condition of the extrudate of S1 was not suitable for many of the tests in this study but was adequate to test MC. TPF samples had MC in the

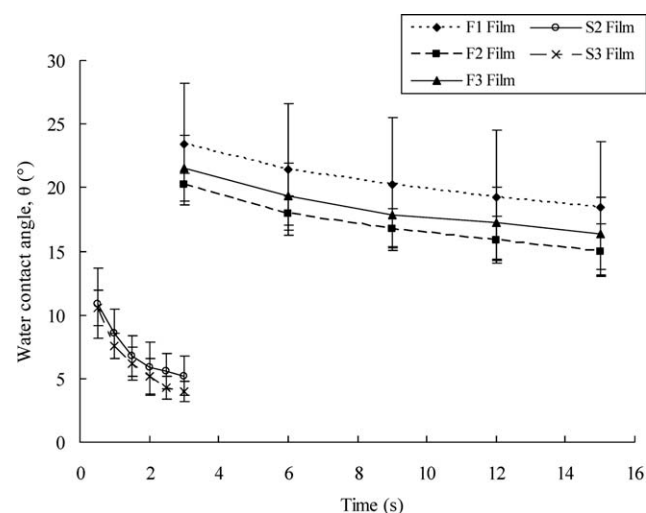


Figure 2 Water contact angle against time on TPF and TPS films.

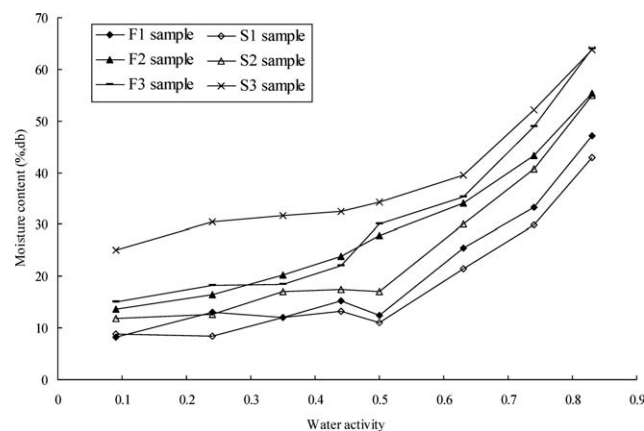


Figure 3 Moisture sorption isotherms of TPF and TPS samples.

range of 11–23%, while TPS had 10–26%, on a wet basis, which was in line with previous findings by Dai et al.,²² who reported that TPS with 30% glycerol contained 13–14% MC after conditioned in 68% RH environment for 20 days. As shown in Table III, the MC of both TPF and TPS samples clearly increased as the amount of plasticizer added increased. The hydrophilic characteristics of plasticizers could be responsible for the increase of MC in the film samples. The increase in glycerol content benefited MC improvement due to the three hydrophilic hydroxyl groups in its molecule.²³ The difference of MC between TPF and TPS films at the same plasticizer level was not obviously clear. F2 had a significant higher MC than the S2 sample, while F1 and S1, and F3 and S3 were not different ($P < 0.05$).

Water solubility index

The WSI of TPS and TPF samples is displayed in Table III. It was possible again to use the S1 extrudate in the testing of WSI. As shown in Table III, the WSI of TPF was larger by $\sim 10\%$ compared with that of TPS, and the difference was consistently observed in every formulation tested. Soluble protein and fiber contained in the flour were ascribed to this increase in WSI. Moreover, there was a small but clear relation between plasticizer content and WSI. The WSI became higher when a larger amount of plasticizer was present in the sample, and this trend was observed in both TPS and TPF samples, which could be due to the high water solubility of plasticizers.

Moisture sorption isotherm

Figure 3 shows the sorption isotherms of all samples. S1 extrudate was used to test sorption isotherm. All samples behaved similarly with MC (d.b) exhibiting a sigmoidal-type adsorption profile, increasing from 10 to 50% with increasing film a_w

from 0.1 to 0.8. The incorporation of higher amounts of glycerol and triethyl citrate appeared to result in a higher MC. In general, the higher the film a_w and the plasticizer content were, the higher the amount of moisture was being adsorbed. Table IV shows the estimated parameters and goodness of fit for the GAB model to the experimental data on moisture sorption isotherm for TPF and TPS samples. The regression analysis had G values below 10 for all the samples (Table IV), so the GAB model was considered to fit all experimental data reasonably well. Rosa et al.,¹² Wang et al.,¹³ and Zhang et al.³ reported similar results for TPS films. Parameter A in GAB model corresponds to the content of monolayer water in the samples, which relates to the stability of the films.²⁴ At monolayer moisture content level, both chemical and microbiological reactions leading to a loss of quality of samples can be neglected.²⁵ Table IV shows the monolayer water content in the film samples was in the range of 7.35–22.06 g/100 g (d.b), which is comparable with results reported in the literatures.^{26,27} Zhang et al.³ reported that pea starch film plasticized by glycerol had 38.96 g/100 g (d.b) monolayer water, which is higher than the current results. Table IV also shows that the monolayer water content clearly increased with increasing plasticizer content, which is in agreement with the observations on moisture content (MC) mentioned above. Another important value derived from GAB is the specific surface area, S_0 . Table IV shows that S_0 of the TPF and TPS samples was from 257.2 to 772.2 $\text{m}^2 \text{g}^{-1}$, increasing with plasticizer content. The increasing trend of the S_0 with plasticizer content indicated that plasticizer loosened the structure of the samples, providing more available surface area for hydrophilic binding. Below the 35% plasticizer level, TPS film had less S_0 value than TPF film, indicating film structure from starch was more compact than from flour. However, once plasticizer content reached up to 35%, the starch film lost its compact structure and became looser than its counterparts. There are some S_0 data reported on food products in literatures,¹² which were in range of 100–200 $\text{m}^2 \text{g}^{-1}$, but few have reported on S_0 for starch film so far.

TABLE IV
GAB Model Constants and G Values for TPF and TPS^a

No. of film	A	B	C	G	S_0 ($\text{m}^2 \text{g}^{-1}$)
F1	8.80	65.63	0.98	9.8	308
F2	15.53	38.24	0.87	3.2	543.6
F3	14.66	95.08	0.93	5.6	513.2
S1	7.35	4.73×10^{63}	1.00	9.5	257.2
S2	10.75	180.40	0.97	8.1	376.2
S3	22.06	4.64×10^{61}	0.78	5.2	772.2

^a S_0 is specific surface area (m^2/g). Mathematical model is displayed in eqs. (3) and (5).

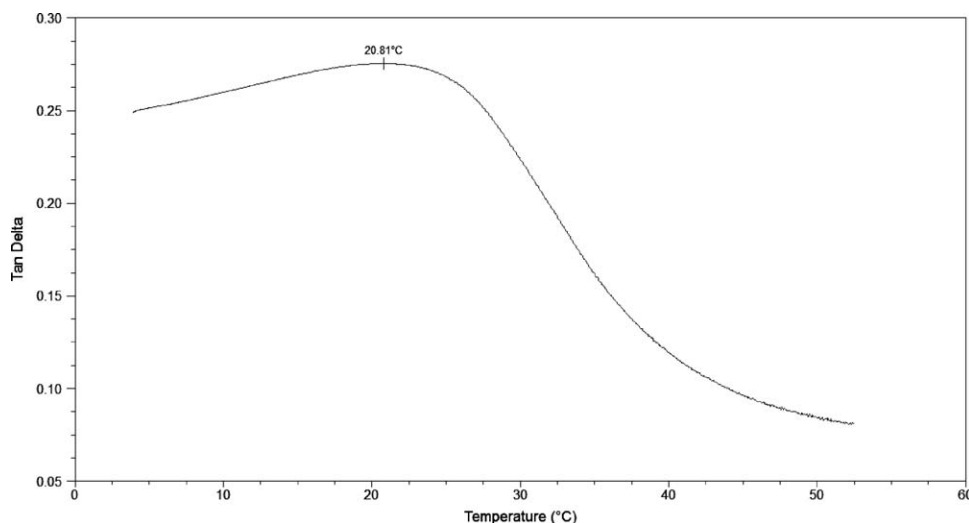


Figure 4 DMA-RH $\tan \delta$ curve of F3 film at 50% relative humidity.

Dynamic mechanical analysis

Figure 4 shows the curve of $\tan \delta$ as a function of temperature ramping from 5 to 50°C for F3 film, being a representative sample. Table III shows that TPF films had T_g in the range of 5–20°C, while T_g of TPS films were greater than 17°C. S1 film had no T_g data due to its unavailability of a film sample. Statistically, the same T_g was observed for F1 and S2 films, F1 and S3 films, as well as F2 and S3 ($P < 0.05$), which verified that the additional components contained in flour contributed to plasticization of TPF films. Chaleat et al.²⁸ reported $\tan \delta$ transition related to α -relaxation for TPS at temperature between –75 and –40°C which is far below present findings.

CONCLUSIONS

The film forming capacity of potato flour by extrusion processing was demonstrated in comparison to potato starch. Properties, such as tensile properties, surface tension, and T_g , were comparative to the conventional starch film despite being less expensive to produce. TPF film surface was less hydrophilic than TPS film, and TPF film was more soluble in water. However, the appearance of TPF film was distinctively different from TPS film. TPF film appeared dark brown, while TPS appeared white or light yellow. TPF also produced unpleasant odor during the extrusion process, while TPS remained relatively odorless. The dark color and unpleasant odor of TPF film may be considered inferior depending on the application and processing facilities. The optimum amount of plasticizer for TPS manufacture was about 30%. However, the optimum amount of plasticizer for TPF might be reduced to around 25% or lower. This conclusion is reasonable considering

that the properties, including mechanical and thermal properties, of TPF film containing 25% plasticizer were similar to those of TPS film containing 30% plasticizer. TPS film has mainly found applications in the meat, poultry, seafood, fruit, vegetable, grains, and candies industries.^{29,30,31} Present results of this study show TPF film also has potential applications in the same areas.

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