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The effect of pea fiber and potato pulp on thermal property, surface tension, and hydrophilicity of extruded starch thermoplastics

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ABSTRACT

The objective of this study was to investigate the effect of the addition of pea fiber and potato pulp on the thermal property, surface tension and hydrophilic character of extruded potato starch films plasticized with glycerol and triethyl citrate. Film samples were prepared from a film device attached with twin screw extruder. The surface tension and hydrophilicity of samples conditioned at 50% relative humidity (RH) were determined through Zisman method and water contact angle measurement, respectively. Addition of fiber or pulp resulted in higher surface energy and hydrophilicity. The thermal property analysis did not indicate that the fiber and pulp had any effect on glass transition temperature (T_g), which was in the range of 20–25 °C. Incorporation of fiber and pulp did not show any effect on the monolayer moisture content and specific surface area of the films. The moisture sorption behaviour of the thermoplastic starch films was also investigated, indicating GAB, Flory-Huggins, and Smith models worked well. Overall analysis exhibited that addition of fiber or pulp increased the hydrophilic character, water wettability, and moisture content of the TPS film. These effects could be related to the addition of hydroxyl groups in the cellulose molecules.

1. Introduction

Mechanical strength is one of the most important properties for the applications of thermoplastic starch (TPS). Due to its low mechanical strength, several approaches have been investigated to improve mechanical properties of TPS, including chemical modification of starch (Reddy & Yang, 2010; Volkert, Lehmann, Greco, & Nejad, 2010), blending starch with biodegradable polymers, such as poly (lactide), poly (caprolactone), poly (propylene carbonate), poly (lactic acid), and poly-3-hydroxybutyrate (Godbole, Gote, Latkar & Chakrabarti, 2003; Ke & Sun, 2000; Preechawong, Peesan, Supaphol, & Rujiravanit, 2005; Wang, Yu, Chang, & Ma, 2007, 2008), and development of the polymer/nanofiller composites (Chung et al., 2010). An additional method to those mentioned above is the use of natural fiber as reinforcement for TPS. Fiber has been reported to successfully enhance the tensile properties of TPS (Azeredo et al., 2009; Panthapulakkal, Zereshkian, & Sain, 2006). Mondragon, Arroyo, and Romero-Garcia (2008) prepared TPS with cellulose microfibrils from husks of corncobs and found the tensile strength of TPS increased from 2.5 to 7.7 MPa with increasing fiber content from 0% to 20% (w/w). Ma, Yu, and Kennedy (2005) did experiments on TPS/micro winceyette fiber composites, and found the increase in fiber content from 0% to 20% (w/w) greatly trebled tensile strength of the TPS composite up to 15.2 MPa. Later on, Ma, Chang, and Yu (2008) obtained similar results on pea starch/carboxymethyl cellulose (CMC) and pea starch/microcrystalline cellulose (MC) composites. The fibers described in the literature for this intention include cellulose nanocrystallites and commercially regenerated cellulose fibers (Curvelo, de Carvalho, & Agnelli, 2001; Ma et al., 2005; Muller, Laurindo, Yamashita, 2009; Soykeabkaew, Supaphol, & Rujiravanit, 2004).

In addition to the mechanical property, other properties such as surface tension, hydrophilicity, moisture sorption isotherm, and glass transition temperature (T_g), are also very important for the applications of TPS. Surface tension is technically significant for TPS capability to be printed, coated, and sealed. In food package, good adhesion in the seal areas is highly desirable. Without adequate adhesion, food may become contaminated with food-borne organisms or extraneous materials (Ozdemir & Floros, 2004). Surface tension is also an important parameter for wettability. High surface tension results in good spreading of a liquid on the surface. TPS usually exhibits high hydrophilic character which is not expected in practical application. Reducing hydrophilicity of TPS is still a big challenge for researchers. Moisture sorption isotherm is a useful method to describe the water adsorption behaviour of TPS. People can predict the moisture content of the TPS by moisture sorption isotherm. Glass transition temperature (T_g) affects TPS properties

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Table 1
Formulations for the different films prepared in study.

Category	Sample no.	Ingredient formulation (%, w/w)			
		Starch	Pea fiber or potato pulp	Glycerol	Triethyl citrate
A (pea fiber)	1	70	0	25	5
	2	65	5	25	5
	3	60	10	25	5
	4	55	15	25	5
B (pea fiber)	1	70	0	27	3
	2	65	5	27	3
	3	60	10	27	3
	4	55	15	27	3
C (potato pulp)	1	70	0	27	3
	2	65	5	27	3
	3	60	10	27	3
	4	55	15	27	3

greatly. TPS demonstrates completely different mechanical properties when it is cooled below or warmed above its T_g. All these properties are critical for TPS's applications which merit investigation. Therefore, unlike most researches, our study concentrated on the effect of fiber on surface tension, hydrophilicity, moisture sorption isotherm, T_g, etc.

Potato pulp can be considered as an alternative to the cellulose fiber for it contains residual cellulose, hemicellulose, starch, and pectin (Mayer & Hillebrandt, 1997). According to Hasa, Tazaki, Ohnishi, and Oda (2006), dried powder of potato pulp obtained from a starch manufacturing plant contains 9.4% moisture, 41.3% fiber, 3.7% crude protein, 0.7% crude fat, 1.9% crude ash, and 36.7% starch. Potato pulp is generated in high quantities during extraction of starch from ground tubers of raw potato, being a waste by-product, traditionally used for animal feed. None literatures report the application of potato pulp in TPS yet.

The objectives of this study are to ascertain how cellulose fiber and potato pulp affect the properties of thermoplastic starch related to its T_g, surface tension and wettability. The work attempts to establish an essential model to describe the moisture sorption behaviour of extruded films prepared from these materials.

2. Materials and methods

2.1. Materials

Potato starch was obtained from Manitoba Starch Products (Carberry, Manitoba, Canada). The composition of the potato starch contains 16.4% moisture and 82.2% total carbohydrates (analysis provided by the manufacturer). Pea fiber (Exlite Fiber, Parrheim Foods, Saskatoon, SK, Canada) was manufactured from the seed coat of the yellow field pea, containing high level in fiber (soluble and insoluble) and mineral content, such as iron and calcium. Potato pulp was prepared from isolation of potato starch in the labs at Guelph Food Research Centre (Guelph, Ontario, Canada), following the procedure of Liu (2002). Glycerol (≥99%) and triethyl citrate (≥99%) were purchased from Sigma–Aldrich Inc., St. Louis, MO, USA, and SAFC Supply Solutions, St. Louis, MO, USA, respectively.

2.2. Preparation of starch films

The ingredient formulations of prepared starch films are shown in Table 1. Three categories were created with 4 samples for each one, which were A, B, and C category, respectively. In each category, starch content decreased and fiber or pulp increased accordingly from No. 1 to No. 4, while the fraction of plasticizer in the total composition was kept constant. Potato starch was mixed with fiber or pulp, glycerol, and triethyl citrate at the concentrations given in the table. Glycerol and triethyl citrate acted as plasticizers, with triethyl citrate also acting as a glidant for improved feeding. All ingredients were weighed into a plastic bag and mixed manually. The blend was manually tumbled carefully for 10 min after mixing. The blend was stored overnight for equilibration. During equilibration, glycerol and triethyl citrate diffused into starch granules and would help extrusion process stability. Before extrusion, the blend was manually tumbled again for 10 min. Extrusion of the blends was done in a mini twin-screw extruder (Micro 15cc Screw Compounder, Model 2005, DSM Xplore, Geleen, Netherlands). Zone temperatures of 125 °C were selected collectively for the feed, metering, compression, and die sections. Processing time was set to 12 min by recirculating the flow stream. Screw speed was 100 rpm. When the films were ready to be 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 films. The films passed through a film device (DSM Film Device, Xplore, Geleen, Netherlands), which calendared, cooled and wound the product at a peripheral speed of 150 mm/min and torque of 19 N-mm. An air knife was used to avoided film distortions while passing through the calendar rolls. After extrusion, the films were cut into 15 cm lengths and conditioned in a chamber having relative humidity (RH) of 52 ± 1% at 22 ± 1 °C for up to 40–50 days. 52 ± 1% RH was achieved with a saturated $Mg(NO_3)_2$ solution, above which the starch film specimens were placed.

2.3. Dynamic mechanical property

Dynamic mechanical property of TPS film was analyzed using a Q800 Dynamic Mechanical Analyzer (TA Instruments-Water LLC, New Castle, Del., USA) working under Advantage for Q Series Version 2.8.0.394 software (TA Instruments-Water LLC) with a DMA-RH accessory and a nitrogen gas cylinder. Film shape was shaped to rectangular with 32.0 mm × 7.0 mm × 0.25 mm ($l \times w \times t$) dimensions. Film tension clamps were used in Multi-Frequency-Strain model with 50% RH inside sample chamber. Strain was applied at 1 Hz with an amplitude of 15 μm. For each analysis, the dynamic mechanical analyzer (DMA) stored values of loss factor, $\tan\delta$ ($\tan\delta = E''/E'$, where E' is the storage modulus, and E'' the loss modulus). The glass transition temperature (T_g) was defined as the peak value of $\tan\delta$. Samples were run in triplicate.

2.4. Surface tension

Surface tension of films was calculated using the Zisman method to determine the so-called critical surface free energy (γ_c). According to Zisman method (Han, Zhang, & Buffo, 2005), the value of γ_c of a solid is equal to the value of surface free energy (γ_l) of a probe liquid being in contact with the solid and for which the contact angle (θ) is zero. For all values of $\gamma_l > \gamma_c$, Zisman and coworkers (Han et al., 2005) found that $\cos\theta$ was usually a monotonic function of γ_l for a homologous series of liquids:

$$\cos\ \theta = a - b\gamma_l = 1 + \beta(\gamma_c - \gamma_l) \quad (1)$$

where a, b, and β are constants. The γ_c value can be obtained from the Fox-Zisman plot ($\cos\theta$ vs. γ_l) by linear extrapolation to $\cos\theta = 1$ from contact angle measurements made with various liquids having different values of γ_l.

Three probe liquids, glycerol (Sigma Chemicals Co., St. Louis, MO), thiodiglycol (2, 2′-thiobisethanol) (Sigma Chemicals Co., St. Louis, MO), and ethylene glycol (EG) (Fisher Scientific, Fair Lawn, NJ) were chosen to measure θ of the film. They have γ_l of 0.064, 0.054, and 0.0477 N/m respectively (Han & Krochta, 1999). A goniometer (EasyDrop standard Drop Shape Analysis System, KRUSS GmbH, Hamburg, Germany) controlled by computer software (v 1.91-01, Software for Drop Shape Analysis, KRUSS GmbH, Hamburg, Germany) was used. A 3 μl drop of a probe liquid was deposited

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 on the film surface were made. All the experiments were done at room conditions of 22 ± 1 °C and 50 ± 2% RH. Fox-Zisman plots of cos θ vs. γ_l for each film were made. The average of ten cos θ values was used to create the Fox-Zisman plot.

2.5. Film hydrophilicity

Initial contact angle measurements with water were performed on the goniometer. A drop of 3 μl distilled water was placed on the surface of each film. For initial contact angle analysis a minimum of five measurements were taken at different positions on the film. The contact angles were measured on both sides of the drop and averaged. During the initial contact angle measurement, the water drop was gradually absorbed into the film and so the contact angle changed continually. As a result, only the first three measurements spanning a 9 s interval were used to estimate the initial contact angle. All contact angle measurements were preformed at ambient conditions of 22 ± 1 °C and 50 ± 2% RH. Water absorption rate was assumed related to the rate of contact angle change, which was described as the slope of θ vs. time. Test time was about 15 s. In order to calculate the slope accurately, linear regression of θ vs. time with $R^2 > 0.8$ was considered. Quadruplicate tests were done for each sample film.

2.6. Moisture content

The moisture content (MC) of the samples was determined gravimetrically by exposing about 1.0 g of each film to 105 °C for 24 h in a forced air oven (Model 750F, Isotemp Standard and Premium Ovens, 700 Series, Fisher Scientific). MC was determined from the percentage of film weight loss after dehydration to original film weight before dehydration. Four replications of each film were measured for given MC values.

2.7. Water solubility

Film samples were cut into small pieces (3.0 mm × 1.6 mm × 0.2 mm, $l \times w \times t$), weighed, and dried in a forced air oven at 105 °C for 24 h. The completely dried film pieces were weighed as W_o, and then put into 50 ml tubes with 25 ml distilled water. The tubes were subjected to occasionally shaking for 24 h at room condition. Then the distilled water was removed out by a pipette. The undissolved film was obtained and put into an aluminium pan for drying in the force air oven at 105 °C for 24 h. After drying, the dried undissolved film was weighed and expressed as W_f. The water solubility (WS) of the film was calculated according to the Eq. (2).

$$WS\,(\%) = \left(\frac{W_o - W_f}{W_o}\right) \times 100 \tag{2}$$

2.8. Moisture sorption isotherm

Eight saturated salt solutions were prepared and placed in 8 sealed desiccators to obtain the specific relative humidity (RH) levels at 22 ± 1 °C, which were LiCl, CH_3COOK, $Mg(Cl)_2$, K_2CO_3, $Mg(NO_3)_2$, NH_3NO_3, NaCl, and KCl for 12, 22, 33, 43, 53, 63, 75, and 85% RH, respectively. The starch films were respectively placed into the preconditioned 8 desiccators with corresponding levels of RH 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. Samples' a_w was measured with a water activity meter (Pawkit, Decagon Devices, Inc., Pullman, WA, USA). Tests were conducted in triplicates, and the average values were used. The moisture isotherm curves were created by plotting MC to a_w. 4 sorption isotherm models, Guggenheim–Anderson–de Bour (GAB), Brunauer–Emmett–Teller (BET), Smith, and Flory-Huggins (Zhang & Han, 2008) listed in Table 2, were established to describe moisture sorption behaviour of the films, among which GAB is adopted as standard equation by the American Society of Agricultural Engineers for describing moisture sorption isotherms (ASAE D245.6 OCT2007). The parameters of these models were estimated using iterative Gauss-Newton method which regress the residuals onto the partial derivatives of the model with respect to the parameters until the parameter estimates converged. Nonlinear regression procedure of SAS software (SAS Inst. Inc., Cary, NC, USA) was applied in the iterative estimation. The goodness of fit of each 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):

Table 2
Moisture sorption isotherm models fitted to experimental absorption isotherm data.

Model name	Model
GAB	$M = ABCa_w/(1 - Ca_w) \times (1 - Ca_w + BCa_w)$
BET	$M = ABa_w/(1 - a_w) \times [1 + (B - 1) \times a_w]$
Smith	$M = A - B \times \ln(1 - a_w)$
Flory-Huggins	$M = A \times \exp(Ba_w)$

M is equilibrium moisture (g water/100 g dry matter); a_w is water activity of the samples. In the GAB model, A is the monolayer moisture content (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; C is a correction factor for the properties of the multilayer with respect to the bulk liquid.

$$G = \left(\frac{100}{n}\right) \sum_{i=1}^{n} \left(\frac{|M_{ai} - M_{pi}|}{M_{ai}}\right) \tag{3}$$

where n is the number of observations, M_{ai} is experimentally determined MC of ith data, and M_{pi} is predicted MC of the ith data by models. A G value lower than 5 corresponds to an excellent fit, a G value between 5 and 10 shows a reasonably good fit, and a G value greater than 10 is considered a poor fit (Rosa, Moraes, & Pinto, 2010; Roy, Gennadios, Weller, & Testin, 2000).

Parameter of A value in GAB equation (Table 2) is monolayer moisture (dry basis) of the film. After A was calculated out in GAB model, the film specific surface area (S_0) was determined by using Eq. (4) (Cassini, Marczak, & Norena, 2006; Rosa et al., 2010). The specific surface area is an important concept in describing the surface characters and water binding properties of the samples.

$$S_0 = M_m \times \left(\frac{N_o \times A_{H_2O}}{M_{H_2O}}\right) = 3.5 \times 10^3 \times M_m \tag{4}$$

where S_0 is the specific surface area ($m^2\ g^{-1}$), 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 (6×10^{23} molecules mol^{-1}), and A_{H_2O} is the area of one water molecule (1.06×10^{-19} m^2).

2.9. Statistical analysis

Data were analyzed by one-way ANOVA using SAS (SAS Institute Inc., Cary, NC, USA) to assess the effects of fiber and pulp on the properties of starch films. A completely randomized full factorial experimental design was used. Mean values with standard deviations were compared using a Tukey's mean difference test at 95% significance level with a null hypothesis of H_0: $\mu_1 = \mu_2 = \ldots = \mu_n$, where μ is a mean of each treatment and n is number of film samples.

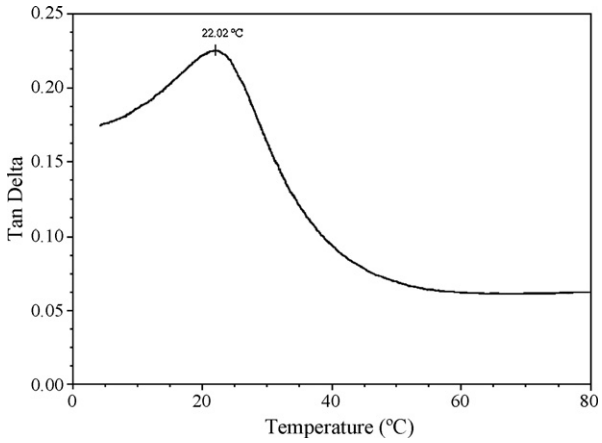

Fig. 1. DMA-RH tan δ curve of C4 film at 50% relative humidity.

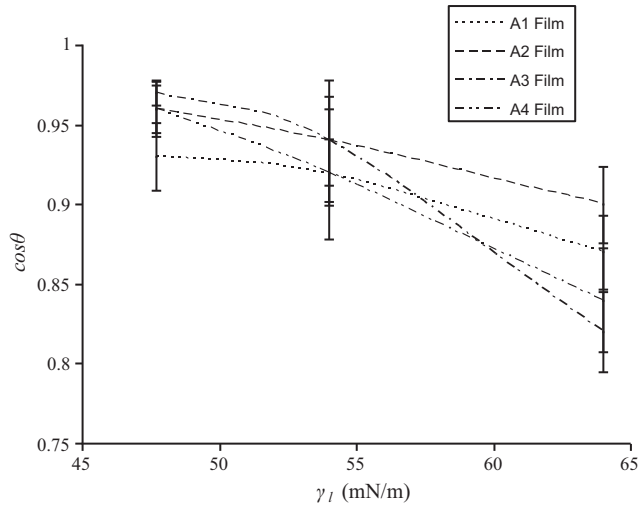

Fig. 2. Fox-Zisman plot of cos θ vs. γ_l for the films in A category. Data on *X*-axis are γ_L for ethylene glycol, thiodiglycol, and glycerol, from left to right, respectively. (···) A1 film, (– –) A2 film, (– · – ·) A3 film, (– ·· –) A4 film. Error bars stand for standard deviation (n = 10).

3. Results and discussion

3.1. Extrusion process and film description

Preliminary experiments performed in our laboratories demonstrated that the plasticizer level should be in the range of 25–35%. Higher amounts of plasticizers led to exudation and lower amounts resulted in difficulties in processing. All films were flat and flexible after extrusion. Without fiber or pulp addition, films of A1, B1, and C1 were white color. After fibers or pulp was added, the films varied in color from being yellowish to dark brown. The fiber was white and pulp had yellowish color. The more fibers or pulp added, the darker the color of the produced film. Films in C group demonstrated improved dimensional stability and more ductility than films in A and B groups.

3.2. Thermal analysis

DMA was used to study the glass transition of TPS film in DMA-RH accessory with 50% RH, in order to avoid moisture escaping from the starch film during the temperature ramping. Fig. 1 shows the curve of tan δ as a function of temperature ramping from 5 to 80 °C for C4 film, being a representative sample. Based on the observed tan δ peak the glass transition temperature (T_g) for the film was considered to be 22.02 °C. Table 3 shows the T_g values of all the films derived from their tan δ peaks. Statistics analysis does not suggest that the addition of fiber and pulp influenced the T_g results significantly. This result makes sense because T_g is primarily determined by plasticizer type and amount for a given polymer matrix. In current experiments, the films had very similar plasticization which was mainly consisted of water, glycerol, and triethyl citrate. Zhang and Han (2006a) tested T_g of pea starch films plasticized by glycerol and found a T_g of −70 °C, which is much lower than current result. Ma et al. (2008) prepared pea starch films with carboxymethyl cellulose and microcrystalline cellulose respectively using a single screw extruder. They found double thermal transitions at −30 °C and 50 °C for the films and contributed this phenomenon to phase separation in the film. Da Roz, Carvalho, Gandini, and Curvelo (2006) obtained similar results with corn starch compositions, which showed two T_g at around −60 °C and 110 °C respectively. They attributed the higher thermal relaxation to the T_g of polysaccharide-rich phase and the lower thermal relaxation to the plasticizer-rich phase of their film.

3.3. Surface tension

Fig. 2 shows a Fox-Zisman plot of cos θ vs. γ_l for films in A group being representative samples. Table 4 shows cosine values of contact angle of the probe liquids, linearity (R^2) of the regression lines of cos θ vs. γ_l shown in Fig. 2, and γ_c. Even though the high hydrophilicity of glycerol, thiodiglycol, and ethylene glycol (EG) could lead to strong interaction between any of these three probe liquids and the starch polymers of the films, R^2 of the regression lines was still greater than 0.85, indicating the linear relationship of γ_l vs. cos θ was reliable. Table 4 shows a trend that γ_c increased with increasing fiber or pulp content. Comparing group A with group B, it was found that B samples had higher γ_c values than A samples. Higher glycerol content in B samples was ascribed to this difference. Glycerol has high surface tension and contributed to the improvement of film surface tension. After fiber content was increased up to 10%, the difference of surface tension between A and B group films was reduced.

Overall, Table 4 shows that starch films had γ_c values in range of 0.030–0.045 N/m, which is very comparative to those of conventional polymers (Han et al., 2005). According to Zisman (Han et al., 2005), liquids with $\gamma_l < \gamma_c$ will spread on the surface of the films, completely wetting the surface. Therefore, it could be deduced that the liquids with $\gamma_l \leq 0.030$ N/m can wet the films successfully. Because fibers and pulp increased the film surface tension, film wettability increased. This bears in mind that γ_c is a critical surface energy of wetting and not equal to the real surface energy of the films. The latter is larger, especially when considering the polar character of starch.

3.4. Film hydrophilicity

The film hydrophilicity was quantitatively characterized by the initial contact angle of water droplets on the film surface. Fig. 3 shows the water initial contact angles of A, B, and C group films. According to the obtained results, the films without addition of fiber or pulp had a water initial contact angle of about 16.5°. With increasing fiber or pulp content, this contact angle reduced gradually to about 6 degrees, indicating an enhancement in hydrophilic character and wettability of the film. This result correlated with the improvement of film surface γ_c with increasing fiber or pulp. Water absorption rate of the starch films was characterized by

Table 3
Film water absorption slope, water solubility, and T_g.

Number of film		T_g (°C)*	Water solubility (%)**	Water absorption slope***
A	1	23.4 ± 1.04[a]	24.0 ± 0.98[ab]	−0.24 ± 0.060
	2	22.4 ± 1.07[a]	23.6 ± 2.61[ab]	−0.29 ± 0.127
	3	23.4 ± 1.33[a]	21.7 ± 0.63[ab]	−0.33 ± 0.089
	4	25.2 ± 1.53[a]	24.8 ± 1.54[a]	−0.35 ± 0.047
B	1	22.4 ± 2.29[a]	21.0 ± 1.17[ab]	−0.16 ± 0.138
	2	20.6 ± 1.78[a]	22.3 ± 2.03[ab]	−0.13 ± 0.040
	3	19.5 ± 1.95[a]	20.8 ± 1.73[ab]	−0.24 ± 0.098
	4	22.8 ± 3.43[a]	20.3 ± 0.41[b]	−0.27 ± 0.127
C	1	18.9 ± 3.66[a]	23.9 ± 0.61[ab]	−0.13 ± 0.110
	2	19.0 ± 3.09[a]	23.2 ± 1.93[ab]	−0.49 ± 0.287
	3	21.3 ± 2.37[a]	23.5 ± 0.52[ab]	−0.41 ± 0.224
	4	21.1 ± 2.60[a]	22.4 ± 1.71[ab]	−0.20 ± 0.03

* Values are means ± standard deviation (n = 3). Same superscripts in the column indicate non-significant difference at P < 0.05.
** Values are means ± standard deviation (n = 3). Different superscripts in the column indicate significant difference at P < 0.05.
*** Values are means ± standard deviation (n = 4).

Table 4
Film probe liquid cos θ, linear regression (R^2), and γ_c (N/m).

Film		EG cos θ	Thiodiglycol cos θ	Glycerol cos θ	R^2	γ_c
A	1	0.93 ± 0.021	0.91 ± 0.041	0.87 ± 0.023	0.95	0.0305
	2	0.96 ± 0.015	0.94 ± 0.038	0.90 ± 0.024	1.00	0.0374
	3	0.97 ± 0.008	0.94 ± 0.028	0.82 ± 0.025	0.96	0.0455
	4	0.96 ± 0.017	0.92 ± 0.021	0.84 ± 0.033	1.00	0.0428
B	1	0.93 ± 0.029	0.93 ± 0.018	0.80 ± 0.050	0.85	0.0420
	2	0.95 ± 0.014	0.94 ± 0.020	0.84 ± 0.041	0.93	0.0420
	3	0.97 ± 0.013	0.94 ± 0.028	0.85 ± 0.045	0.98	0.0445
	4	0.97 ± 0.009	0.96 ± 0.010	0.87 ± 0.045	0.93	0.0444
C	1	0.93 ± 0.033	0.90 ± 0.023	0.82 ± 0.052	0.99	0.0380
	2	0.94 ± 0.019	0.92 ± 0.035	0.84 ± 0.050	0.97	0.0389
	3	0.95 ± 0.031	0.90 ± 0.052	0.77 ± 0.078	0.99	0.0438
	4	0.95 ± 0.032	0.92 ± 0.044	0.80 ± 0.067	0.95	0.0437

Values are means ± standard deviation (n = 10).

water absorption kinetics which was calculated by the measurement of the slope of water θ vs. time. Fig. 4 indicates the relationship between water θ and time, with A films being representative samples. Table 3 shows the regression slopes of water θ vs. time for all films. Table 3 demonstrates the slope decreased with increasing fiber and pulp content, indicating the water absorption rate increased with increasing fiber or pulp content.

3.5. Moisture content

Fig. 5 shows the films had 20–25% of MC. MC increased slightly with increasing the fiber and pulp content, indicating addition of fiber and pulp favoured the polar interaction of film with water molecules. This result corroborates the behaviour previously observed in relation to surface hydrophilicity. However, it is opposite to the observation of Curvelo et al. (2001), who reported that incorporation of cellulose fiber decreased the water sorption of TPS. Fig. 5 also shows that A group films had lower MC than B and C group films. This decrease in MC should be ascribed to the difference of glycerol concentration in the film formulations. B and C group films contained 2% more glycerol than A group films. This result was in agreement with Preechawong et al. (2005), Zhang and

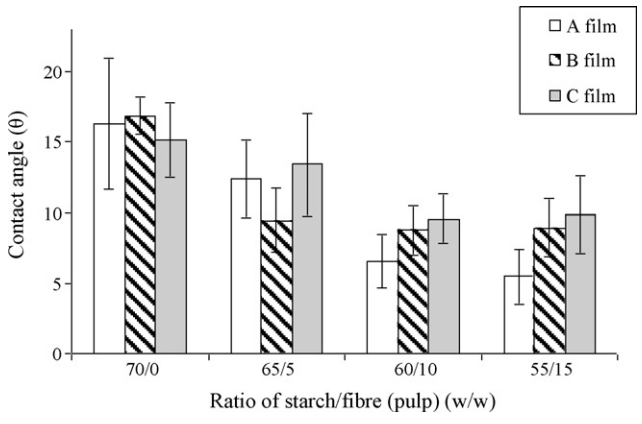

Fig. 3. Water contact angles of the films. Error bars stand for standard deviation (n = 5).

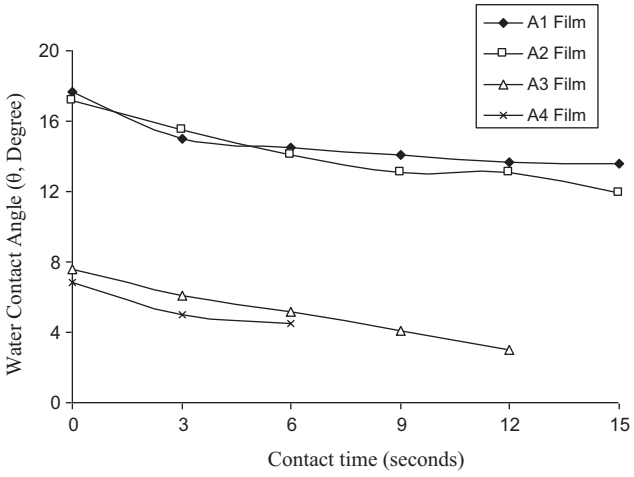

Fig. 4. Regression of water contact angle vs. time of the films in A Category.

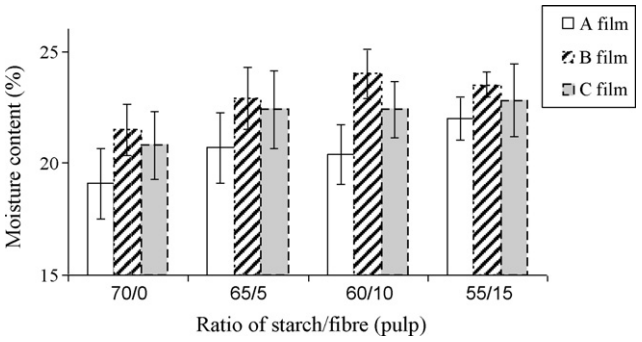

Fig. 5. Moisture content of the films. Error bars stand for standard deviation ($n = 4$).

Han (2006a,b, 2008), and Koch, Gillgren, Stading, and Andersson (2010), who reported that glycerol could cause a higher MC in starch film, and believed that glycerol has a strong capacity to hold water molecules around it.

3.6. Water solubility

Potential application of the starch-based film may require the water solubility or water insolubility. In case of encapsulation of food or additives, water solubility might be expected (Bertuzzi, Armada, & Gottifredi, 2007). But in case of general food packaging, water insolubility is necessary (De Moura, Avena-Bustillos, Mchugh, Krochta, & Mattoso, 2008). Table 3 shows the water solubility of the films. The water solubility of the films ranged from 20 to 25%. Only A4 and B4 films showed differences statistically. All other films exhibited the same water solubility, indicating the addition of fiber and pulp had limited effect. Shen, Wu, Chen, and Zhao (2010) prepared potato starch films and tested the water solubility also. They found 13–14% solubility for the films, which is much lower than the current result. This difference can be attributed to the difference of film preparation method. Shen et al. (2010) prepared their films by the solution casting method in which glycerol was 3% of starch (w/w, dry basis). Current films were prepared with 30% plasticizer, which could lead to higher solubility in the water.

3.7. Moisture sorption isotherm

The moisture sorption characteristic of the films is important for predicting the stability of the films during storage, since the shelf life of the films in different storage conditions is related to their moisture uptake. Fig. 6 shows the equilibrium moisture content (EMC) of films at different a_w at $22 \pm 1\,^{\circ}C$. The average of EMC from a_w of 0.1 to 0.85 ranged from 10% to 60%. The EMC increased with increasing a_w. All the samples exhibited similar behaviour. In addition, Fig. 6 presents sigmoidal-type curves of the sorption profiles, suggesting Type II isotherm occurred (Brunauer, 1945). Type II isotherm happens when more water condenses on the surface over the water monolayer.

Table 5 show the estimated parameters and goodness of fit of the models, listed in Table 2, to the experimental data. Flory-Huggins, Smith, and GAB models had G values below 10, indicating they fitted the experimental data reasonably well. According to Kaymak-Ertekin and Gedik (2004), a model's fit is satisfactory for practical purpose when G is less than 10. BET model had G values above 20, showing it was not a good model to describe sorption behaviour of the films. Labuza (1968) figured out that BET is valid only in the range of 10–50% RH, because it does not take into account water effect on structural change of the films, which usually occur at above 70% RH. GAB model is an extension of the BET model with a correction factor, C, for the structural changes of starch films. With C factor, GAB model is valid in almost entire range of RH and fitted current experimental data very well. This was also confirmed by Zhang and Han (2008), who found GAB fitted the sorption isotherm data of pea starch films very well.

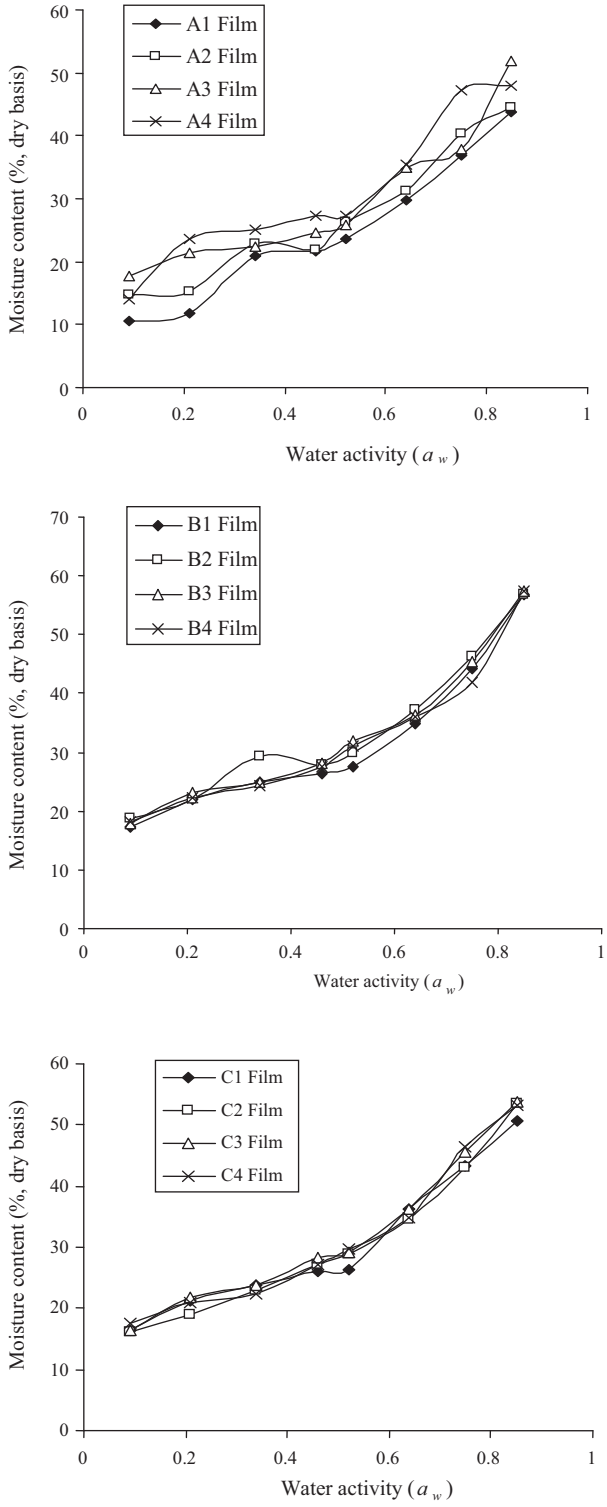

Fig. 6. Moisture sorption isotherms of the films, indicating sigmoidal – type sorption behaviour.

Flory-Huggins and Smith models also fitted the experimental data very well (Table 5). Flory-Huggins fits the moisture isotherm in the case of stronger water–water interaction than the water–starch matrix interaction. Once starch film successfully absorbed a water molecule onto one of its primary adsorption sites, the adsorbed

Table 5
Flory-Huggins, Smith, BET, and GAB model constants and *G* values (mean relative deviation modulus) for the films.

No. of film		Flory-Huggins			Smith			BET			GAB[a]				
		A	B	G	A	B	G	A	B	G	A	B	C	G	S_0
A	1	9.5	1.8	5.7	10.0	18.7	7.2	8.3	-3.9×10^{68}	22.7	16.3	15.7	0.8	7.1	569.36
	2	11.8	1.6	6.3	12.9	17.6	5.9	8.8	-5.9×10^{64}	28.2	16.2	53.0	0.8	6.4	566.96
	3	13.3	1.5	8.4	13.2	18.0	8.1	9.6	7.1×10^{62}	27.2	16.0	-1.9×10^{72}	0.8	4.8	561.70
	4	14.5	1.4	8.9	16.1	18.7	9.3	9.9	-2.5×10^{62}	30.6	20.7	32.2	0.7	7.0	723.48
B	1	13.3	1.6	8.8	14.8	21.2	5.3	10.4	-4.4×10^{62}	25.5	16.7	-4.7×10^{61}	0.8	3.8	583.90
	2	15.1	1.5	7.1	16.9	20.8	4.2	10.8	-2.2×10^{61}	28.1	18.9	173.7	0.8	3.7	662.58
	3	14.5	1.6	5.7	16.2	20.2	2.6	10.7	-6.9×10^{67}	27.2	18.4	162.4	0.8	2.4	645.66
	4	14.1	1.6	6.7	15.9	20.6	3.4	10.5	-6.9×10^{65}	26.4	17.4	3.5×10^{4}	0.8	2.8	607.30
C	1	13.6	1.5	5.5	15.1	19.3	7.0	9.8	-3.2×10^{65}	28.4	17.7	91.0	0.8	4.2	618.48
	2	12.8	1.6	3.8	14.1	20.7	0.9	10.1	-1.8×10^{70}	26.1	17.2	79.2	0.8	1.1	603.02
	3	13.9	1.6	3.9	15.3	20.7	3.0	10.3	4.2×10^{70}	27.8	18.6	63.7	0.8	2.3	652.02
	4	13.5	1.6	5.6	15.0	20.7	3.6	10.3	1.5×10^{64}	27.7	17.7	127.1	0.8	2.8	619.84

[a] In GAB model, *A* is the monolayer moisture content (water g/100 g, dry basis). S_0 is specific surface area (m^{-2}/g).

water molecule became a secondary adsorption site which can add other molecules of water due to the hydrogen bonds. So, it could be deduced from the good fit of Flory-Huggins model that the interaction between the water and water became a major driving force of the adsorption process, resulting in accelerated water uptake at higher RH. The Smith equation is an empirical model. It has been proven to be useful in describing the sorption isotherm of biological materials such as starch and cellulose (Hossain, Bala, Hossain, & Mondol, 2001).

Not only can the GAB model describe sorption behaviour, but also it can provide data on the monolayer water of the films. This data is valuable because it relates to the stability of the films (Diab, Biladeris, Gerasopoulos, & Sfakiotakis, 2001). At monolayer moisture content level, the rates of film quality loss resulting from chemical reaction and microbial growth are negligible (Zimeri & Kokini, 2002). The monolayer moisture value can be estimated from the parameter *A* in GAB model. Table 5 shows that the monolayer water of the films was in range of 16–20 g/100 g (d.b), indicating the films were stable at this moisture content level. This monolayer moisture data is comparative to other biopolymers reported in the literatures (Biliaderis, Lazaridou, & Arvanitoyannis, 1999; Roy et al., 2000). In Table 5, there is no evidence showing incorporation of fiber and pulp affected the monolayer moisture content of the films. Table 5 also shows the specific surface area, S_0, values of film samples calculated by Eq. (4) using the monolayer moisture values, resulting in 560–720 $m^2\ g^{-1}$, respectively. Table 5 does not indicate that incorporation of fiber and pulp had any effect on the availability of specific surface area for hydrophilic binding. These S_0 values were higher than the data of 100–200 $m^2\ g^{-1}$ for common food products (Rosa et al., 2010) and 267 $m^2\ g^{-1}$ for chitosan at equilibrium temperature of 4 °C (Kablan, Clement, Francoise, & Mathias, 2008), and comparative to the data of 450–700 $m^2\ g^{-1}$ reported by Rosa et al. (2010) for desorption of chitosan at equilibrium temperatures from 20 to 60 °C. No report of specific surface area for starch films is available so far in literatures.

4. Conclusions

Addition of either pea fiber or potato pulp was found to have no effect on the T_g of a thermoplastic starch film, which was in the range of 20–25 °C. However, moisture content of the film was observed to increase significantly with increasing fiber or pulp content. Moreover, surface tension and hydrophilicity of the films increased with increasing fiber or pulp content, indicating water would more easily wet or spread on the surface. GAB, Flory-Huggins and Smith models were found to reasonably describe the moisture sorption behaviour of the films, while BET model did not, indicating the starch matrix structure greatly changed when the films were stored in high RH environment.

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