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Effects of surfactants on the functional and structural properties of kudzu (*Pueraria lobata*) starch/ascorbic acid films

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ABSTRACT

The aim of this research was to evaluate the effects of surfactants (span 80, tween 20 or the blend of above surfactants at the ratio of 1:1) on the properties of kudzu starch/ascorbic acid films. Each surfactant decreased surface tension of the film-forming solution and delayed the release of ascorbic acid from film to water. Tween 20 improved the wettability of film-forming solutions on both glass and paraffin wax substrates, and promoted the formation of V-type crystal in the films. The film's surface morphology was different depending on the surfactant types. The film containing only tween 20 showed higher flexibility, water content and solubility, lower mechanical strength, and comparable water vapor permeability when compared with the film containing only span 80. The film adding blended-surfactant was not only without better morphology, wettability and mechanical properties but had the worst water barrier ability as regarding the film containing single surfactant.

1. Introduction

There is an increasing interest in edible films and coatings nowadays, which partly due to the need of renewable packaging resources and improved food preservation. Edible films and coatings formed by natural biopolymers can act as barriers of mass transfers (such as water vapor and gases), mechanical protections against deterioration and even carriers of functional additives (such as antioxidants, and antimicrobial agents), and thus can effectively extend the shelf-life of food products (Chen, Kuo, & Lai, 2010). Starch is one of the most promising raw materials to produce edible films and coatings due to its abundance, low cost, biodegradability, renewability and film-forming ability (Avérous, Fringant, & Moro, 2001). The potential of starch as a material for edible films has been widely known (Bergo et al., 2008; Bertuzzi, Castro Vidaurre, Armada, & Gottifredi, 2007; Talja, Heleïn, Roos, & Jouppila, 2007). Kudzu (*Pueraria lobata*) is a traditional medical plant cultivated in China which is rich in starch in its root. As kudzu starch contains a number of amino acids and various minor constituents (Geng, Zongdao, & Yimin, 2007; Van Hung & Morita, 2007), it can be served as a functional food source to make edible films and coatings.

Ascorbic acid is one of the most extensively used addictives which is added to foods for mainly two purposes: as a vitamin supplement to reinforce dietary intake of vitamin C and as an antioxidant to protect the quality of foods (Bastos, Araújo, & Leão, 2009). Our preliminary experiments indicated that the addition of ascorbic acid enhanced the water sorption ability and decreased the water barrier ability and mechanical strength of kudzu starch films, which was consistent with the previous reports (Bastos et al., 2009; Seacheol & Krochta, 2007).

Surfactant is a kind of amphiphilic substance, which possesses hydrophilicity and hydrophobicity simultaneously (Chen, Kuo, & Lai, 2009). The lipophilic part of the surfactant is prone to be in a non-polar environment; whereas the hydrophilic part tends to be in a polar environment. The balance between these two parts could regulate a surfactant's functionality at interfaces which impacts on the properties of the resulting films. It has been reported that surfactant was incorporated into film formulation in order to reduce surface tension of the film-forming solution, and improve the wettability and adhesion ability of film (Rodríguez, Osés, Ziani, & Maté, 2006). Besides, surfactant is always applied in starch-containing food to retard starch retrogradation as it can interact with the amylose to form complexes (Mondragón, Arroyo, & Romero-García, 2008). Several surfactants have been used to produce edible films and coatings including both ionic and non-ionic kinds (Andreuccetti, Carvalho, Galicia-García, Martínez-Bustos, & Grosso, 2011; Bravin, Peressini, & Sensidoni, 2004; Morillon, Debeaufort, Blond, Capelle, & Voilley, 2002). In particular,

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Table 1
Composition of kudzu starch/ascorbic acid film formulations (g/100 ml solution) and hydrophilic–lipophilic balance (HLB) of the surfactants.

Formulations	Kudzu starch	Glycerol	Span 80	Tween 20	Ascorbic acid	HLB of surfactants
KA	3	0.9	0	0	0.5	–
KAS	3	0.9	0.1	0	0.5	4.3
KAT	3	0.9	0	0.1	0.5	16.7
KAST	3	0.9	0.1	0.1	0.5	10.5

span 80 and tween 20 are two widely used surfactants which have different Hydrophilice Lipophilic Balance (HLB). Rodríguez et al. (2006) stated that water vapor permeability (WVP), mechanical properties and wettability of potato starch films were affected more or less by the dosage of span 80 and tween 20. Although the effects of the addition of surfactants on relevant properties of varied films were investigated (Andreuccetti, Carvalho, & Grosso, 2010; Chen et al., 2009; Villalobos, Chanona, Hernández, Gutiérrez, & Chiralt, 2005; Villalobos, Hernández-Muñoz, & Chiralt, 2006), there is little work regarding the influence of surfactants on properties of active packaging, especially on the wettability of film-forming solution and the release of active ingredients.

In present study, the effect of surfactant on the surface tension and wettability of kudzu starch/ascorbic acid film-forming solution, as well as on the release behavior of ascorbic acid into water, the microstructure, crystal structure, surface hydrophobicity, mechanical properties, water vapor permeability and solubility of film were evaluated.

2. Materials and methods

2.1. Materials

Kudzu starch (*Pueraria lobata*, water content: 14.26% total weight, protein: 0.94%, db, lipid: 0.06%, db, ash: 0.14%, db, amylose: 30.01%) was purchased from Xichuan Chunyu Geye Biotechnology Co., Ltd. (Henan, China). Glycerol ($C_3H_8O_3$), tween 20 ($C_{58}H_{113}O_{26}$), span 80 ($C_{24}H_{44}O_6$), ascorbic acid ($C_6H_8O_6$), magnesium nitrate ($Mg(NO_3)_2$), phosphorus pentoxide (P_2O_5), anhydrous calcium chloride ($CaCl_2$) and sodium chloride (NaCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Experimental design

Four film-forming solutions were obtained using kudzu starch at 3.0% (w/v), glycerol at 0.9% (w/v), span 80 and tween 20 at 0.0% or 0.1% (w/v), and ascorbic acid at 0.5% (w/v). The composition of edible film formulations (g/100 ml solution), and corresponding HLB of the surfactants (Rodríguez et al., 2006) were given in Table 1.

2.3. Film preparation

Aqueous kudzu starch solutions were prepared and heated with stirring at 100 °C for 15 min; meanwhile, glycerol was added. Then, the solutions were mixed with surfactants when needed. After cooling down to 40 °C (ca. 0.5 h) with stirring, the solutions were incorporated with ascorbic acid. Afterwards, the solutions (KA: kudzu starch solution with ascorbic acid; KAS: kudzu starch solution with ascorbic acid using span 80 as surfactant; KAT: kudzu starch solution with ascorbic acid using tween 20 as surfactant; KAST: kudzu starch solution with ascorbic acid using blended span 80 and tween 20 as surfactant) were homogenized using an APV 1000 homogenizer (APV, Silkeborg, Denmark) for 10 min at a pressure of 150,000 kPa. Immediately after, a vacuum (vacuum degree 6×10^{-2} Pa) was used to remove air bubbles in the solutions.

Films were cast by pouring 200 ml of solutions onto the leveled glass plates (25 × 25 cm) and dried at 25 ± 1.5 °C for at least 16 h until the weights approached to constant values. Then, the films were carefully peeled from the plates and stored for 48 h in desiccators containing $Mg(NO_3)_2$ saturated solutions (53% relative humidity, RH) at 25 °C before further tests.

2.4. Properties of film-forming solutions

2.4.1. Surface tension analysis

Surface tension of film forming solution was measured with a BYZ-1 automatic Tensiometer (Shanghai Heng Ping Instrument Manufactory, Shanghai, China). All measurements were made at 25 °C and three replications were performed in each case.

2.4.2. Contact angle

The static contact angles for a drop of film-forming solution applied on the clean leveled surface of sized glass and paraffin wax substrates were measured with a DSA 30 Contact Angle Analyzer (Kruss Co., Germany). Six replicate determinations were carried out for each sample, and the results were averaged.

2.5. Characterization of the films

2.5.1. Release test

Release test was carried out based on the method described by Flores, Conte, Campos, Gerschenson and Del Nobile (2007) and Gemili, Yemenicioglu, and Altinkaya (2010) with some modifications. Film discs (1.4 cm in diameter and 0.1 mm in width) were introduced into weighing bottles (70 × 35 mm) containing 60 ml of distilled water and stirred magnetically at 150 rpm with a 2 cm long Teflon coated rod. A 1 ml of samples at different time periods (0.5, 1, 1.5, 3, 6, 7, 9, 15, 20, 25, 30, 45, and 60 min) at 25 °C were taken out and analyzed for 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical-scavenging activity. All measurements were performed in triplicate.

2.6. DPPH test

A 1 ml of solution being taken out of the weighing bottle was mixed vigorously with 4 ml of 75 μmol/L DPPH in methanol and the mixture was placed at 25 °C in the dark for 60 min. The absorbance of the mixture at 516 nm was measured using a spectrophotometer (UV-2100, UNICO (Shanghai) Instruments Co., Ltd., Shanghai, China). Percentage inhibition of DPPH free radical was then calculated and converted to ascorbic acid equivalent by using standard curve.

2.7. Determination of diffusion coefficients

Assuming uniform initial ascorbic acid distribution and negligible external resistance, the release behavior of ascorbic acid can be described by Fick's second law for an infinite slab (Crank, 1975). The

solution of the Fick's second law with constant boundary conditions in present study is as follows (Ozdemir & Floros, 2001).

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\frac{(2n+1)^2}{L^2}\pi^2 Dt\right] \quad (1)$$

where M_t is the amount of released ascorbic acid content at time t (g ascorbic acid/g film), M_∞ is the amount of released ascorbic acid content until equilibrium (g ascorbic acid/g film), L is the thickness of film (m), D is diffusion coefficient (m^2/s), t is releasing time (min), and n is the positive integer.

2.7.1. Scanning electron microscopy

The films were conditioned in desiccators containing P_2O_5 (25 °C) for 7 days and then fractured in liquid nitrogen. The fractured samples were coated with gold in a LDM-1000A sputter coater (Shanghai Yong Lin Electronics Equipment Co., Ltd., Shanghai, China) at 3–5 mA for 150 s. Morphological observations of the film surface and internal structures were carried out using a field emission scanning electron microscope (Zeiss, Germany) at 5 kV.

2.7.2. X-ray diffraction

X-ray diffraction (XRD) of the film was carried out with an XRD-6000 X-ray diffractometer (Shimadzu Co., Japan) at 25 °C. It was equipped with a copper tube operating at 40 kV and 30 mA, a 1° divergence slit, a 1° scatter slit and a 0.3 mm receiving slit. XRD patterns were recorded in an angular range of 5–35° (2θ) with scanning rate of 5° min^{-1}.

2.7.3. Surface hydrophobicity and wettability

The surface hydrophobicity and wettability of the films were evaluated by measuring the contact angle of distilled water droplet deposited on the film surface using a DSA 30 Contact Angle Analyzer (Kruss Co., Germany) equipped with a CCD camera.

2.7.4. Water content

Films were weighed before and after dried in an oven at 105 °C for 24 h. Water content was calculated as follows:

$$\text{Water content} = \frac{M_0 - M}{M} \quad (2)$$

where M_0 is the initial film mass (g) and M is the dry weight (g). Water content is expressed as g H_2O/g dry solids.

2.7.5. Water vapor permeability

Water vapor permeability (WVP) was determined gravimetrically based on the method described by Talja et al. (2007) with some modifications. Thickness of each film was measured at five randomly chosen points using a micrometer (with an accuracy of 0.02 mm). The films were sealed onto permeation cells (1384.74 × 25 mm^3) filled with granular (Φ < 2 mm) anhydrous calcium chloride. The permeation cells were then placed in desiccators containing saturated NaCl solutions, providing RH gradients of 0/75% at 25 °C. The permeation cells were weighed as a function of time until changes in the weight were recorded to be the nearest 0.001 g. WVP was calculated as follows:

$$WVP = \frac{mL}{At\Delta P} \quad (3)$$

where m is the weight of water permeated through the film (g), L is the thickness of the film (m), A is the permeation area (m^2), t is the time of permeation (s), and ΔP is water vapor pressure difference across the film (Pa). Five repetitions were made for each test.

2.7.6. Mechanical properties

The mechanical properties were determined according to the method described by Chen et al. (2010) with some modifications and were carried out using a TA-XT2i Texture Analyzer (Stable Microsystems Ltd., UK). Eight repetitions were performed for each sample.

Films were cut into strips (20 × 80 mm) and mounted between the tensile grips (A/TG). Initial grip separation was 50 mm and crosshead speed was 0.8 mm s^{-1}. Tensile strength (TS, MPa) and elongation at break (EB, %) were then determined.

2.7.7. Film solubility

A modified method from Andreuccetti et al. (2011) was used to measure film solubility. Film sheets (20 × 20 mm) were dried at 70 °C for 24 h in a vacuum oven (Shanghai Yi Heng Technology Co., Ltd., Shanghai, China) to get the initial dry mass. Then the films were placed in 50 ml beakers containing 30 ml of distilled water. The beakers were covered with plastic wraps and stored at 25 °C for 24 h. Water remaining in the beakers was discarded and the residual film pieces were rinsed gently with distilled water. The residual film sheets were dried at 70 °C in a vacuum oven to determine the dry mass. Three measurements were taken for each treatment. Film solubility was calculated using the following equation:

$$\text{Film solubility} = \frac{(M_{before} - M_{after})}{M_{before}} \times 100\% \quad (4)$$

where M_{before} and M_{after} are the dry mass of the film before and after the solubility test, respectively (g).

2.8. Statistical analysis

A computer program, based on the theoretical analysis (Eq. (1)) was written in SAS (version 9.2, SAS Institute, Inc., Cary, USA) to determine the ascorbic acid diffusion coefficients in films. Statistical analyses were performed by SAS software package. Data were analyzed by one-way analysis of variance (ANOVA). Duncan's multiple range tests were used to assess the differences of means, and differences were considered significant at $P < 0.05$.

3. Results and discussion

3.1. Surface tension of film-forming solution

Surface tension of kudzu starch/ascorbic acid solution without surfactant was ca. 61.5 mN/m in present study (Table 2). As expected, the presence of surfactant significantly ($P < 0.05$) decreased the surface tension of the film-forming solution. This trend was similar with previous results reported by Rodríguez et al. (2006), who found that tween 20 could diminish surface tension of potato starch film-forming solution even at low concentration (0.01%), but span 80 needed higher amounts (0.1%) to be effective; while high surfactant concentration (0.1%) resulted in significantly ($P < 0.05$) lower surface tension values for all surfactants.

3.2. Contact angle of film-forming solution

Wetting behavior of film-forming solution on food surface affects its adhesion ability on food product, which can be reflected from its contact angle on food surface. The major factors affecting the contact angle of a liquid droplet on a certain solid surface were the droplet properties and the liquid–solid interactions. In order to investigate the wettability of film-forming solutions on the surfaces of different polar solids, glass was chosen as hydrophilic solid and paraffin wax was chosen as hydrophobic solid in present study. The static contact angles of film-forming solutions on glass and paraffin wax substrates were measured by the sessile drop technique.

All of the contact angle values on glass substrates were well below 90°, indicating the solutions to be rather hydrophilic. The

Table 2
Properties of kudzu starch/ascorbic acid film-forming solutions.[a,b]

Solution	Surface tension (mN/m)	Contact angle on glass (°)	Contact angle on paraffin wax (°)
KA	61.5 ± 0.90^{A}	27.0 ± 1.02^{B}	113.3 ± 3.93^{A}
KAS	42.7 ± 1.57^{B}	38.3 ± 3.64^{A}	109.8 ± 2.50^{A}
KAT	42.8 ± 0.31^{B}	22.1 ± 0.41^{C}	101.2 ± 2.15^{B}
KAST	43.3 ± 1.11^{B}	36.1 ± 0.50^{A}	100.7 ± 1.51^{B}

[a] Data were shown in mean ± standard deviation.
[b] Different superscript letters in the same column indicated significant differences ($P < 0.05$).

contact angle of KAT solution was obviously ($P < 0.05$) smaller than other film-forming solutions, which displayed the promoting effect of tween 20 on the wettability of kudzu starch/ascorbic acid solution on glass substrate. However, the contact angle values of span 80-containing solutions were significantly ($P < 0.05$) higher than that of the control solution. In addition, despite the lowest surface tension of KAST solution (35.3 ± 1.11 mN m^{-1}), its contact angle on glass substrate was similar with that of KAS solution. It can be inferred, therefore, that the hydrophobic effect of span 20 was more potent in film-forming solutions.

As for the contact angle on paraffin wax substrate, all values obtained were higher than 90°. Although the adhesion of film-forming solution on paraffin wax was relatively poor, each surfactant addition decreased the contact angle value. The improvement in the affinity of film-forming solution on paraffin wax surface may be resulted from the hydrophobic interactions between hydrophobic groups of surfactants and the paraffin wax substrate. Despite span 80 was more lipophilic than tween 20, the contact angle of KAS solution was obviously greater ($P < 0.05$) than that of KAT solution, which may be due to the insolubility of span 80 and its consequent unhomogeneous distribution in water. Moreover, there were no significant ($P > 0.05$) differences between the contact angles of KAT and KAST solutions.

From the experimental data, it was clear that tween 20 was a more effective surfactant to improve the wettability of kudzu starch/ascorbic acid solution on the two substrates in present study.

3.3. Ascorbic acid release and diffusion coefficients

During the release tests, water molecules could penetrate into the hydrophilic kudzu starch matrix and facilitated the macromolecular mobility of the film network. Thereafter, the entrapped ascorbic acid would diffuse from the matrix into the outer solution until a thermodynamic equilibrium was reached (Flores et al., 2007). Theoretical ascorbic acid release curves fitted to the experimental data were shown in Fig. 1. The excellent conformity of the predicted values to the experimental data suggested the suitability and accuracy of the model in describing ascorbic acid release process. Diffusion coefficients of ascorbic acid released from films are summarized in Table 3. The mean diffusion coefficients of water-soluble ascorbic acid from KA, KAS, KAT and KAST films to water were 2.22, 0.97, 1.61, and 0.87×10^{-11} m^2 s^{-1}, respectively, which implied the postponing impact of the surfactant. The hydrophobic

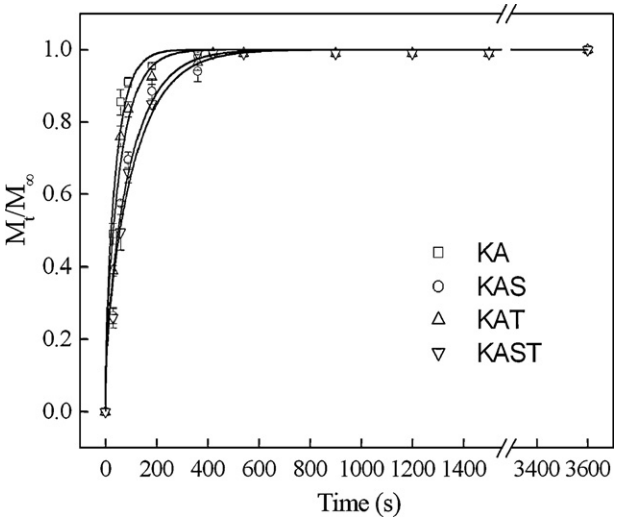

Fig. 1. Release kinetics of ascorbic acid from kudzu starch film into water. The curves were the fitting of Eq. (1) to the experimental data.

span 80 could retard water absorption of the film, leading to the more distinctly decrease of diffusion coefficient. Whereas, tween 20 was more hydrophilic than span 80, its delaying effect was less obvious. The comparable diffusion coefficients of ascorbic acid in present study with those of other active compounds from different natural biopolymers (Flores et al., 2007; Ozdemir & Floros, 2001; Sebti, Blanc, Carnet-Ripoche, Saurel, & Coma, 2004; Zactiti & Kieckbusch, 2009) into water indicated that kudzu starch films can be used to carry and deliver active substances.

3.4. Scanning electron microscopy

The KA film and films containing tween 20 (Fig. 2A, C, and D) presented continuous and compact surfaces without pores or cracks, moreover, the surface of the KAT film was more homogeneous and smooth. When only the water-insoluble span 80 was added to the film formulation, small globules were found on the surface of the formed film (Fig. 2B), demonstrating the migration of span 80 to the film surface.

The cross section morphology can reveal internal structures of films and contribute to better knowing the film-forming behaviors

Table 3
Other properties of kudzu starch/ascorbic acid films.[a,b]

Film	Ascorbic acid diffusion coefficient ($\times 10^{-11}$ m^2/s)	Contact angle of water droplet (°)	Mechanical properties		Water content (%)	WVP ($\times 10^{-11}$ g m^{-1} s^{-1} Pa^{-1})	Solubility (%)
			TS (MPa)	EB (%)			
KA	2.22 ± 0.14^{A}	35.9 ± 4.73^{B}	4.00 ± 0.47^{A}	32.59 ± 4.06^{B}	21.5 ± 0.52^{AB}	5.25 ± 1.40^{B}	36.9 ± 1.01^{C}
KAS	0.97 ± 0.007^{C}	44.8 ± 1.12^{A}	3.51 ± 0.21^{B}	37.10 ± 1.66^{B}	19.0 ± 0.75^{B}	5.19 ± 0.85^{B}	38.8 ± 1.03^{BC}
KAT	1.61 ± 0.095^{B}	31.0 ± 1.67^{C}	2.59 ± 0.10^{C}	53.92 ± 3.82^{A}	23.1 ± 0.45^{A}	4.88 ± 0.94^{B}	40.5 ± 1.35^{AB}
KAST	0.87 ± 0.056^{C}	23.9 ± 0.29^{D}	2.18 ± 0.30^{D}	36.60 ± 6.91^{B}	19.7 ± 3.10^{B}	9.27 ± 1.19^{A}	41.5 ± 1.73^{A}

[a] Data were shown in mean ± standard deviation.
[b] Different superscript letters in the same column indicated significant differences ($P < 0.05$).

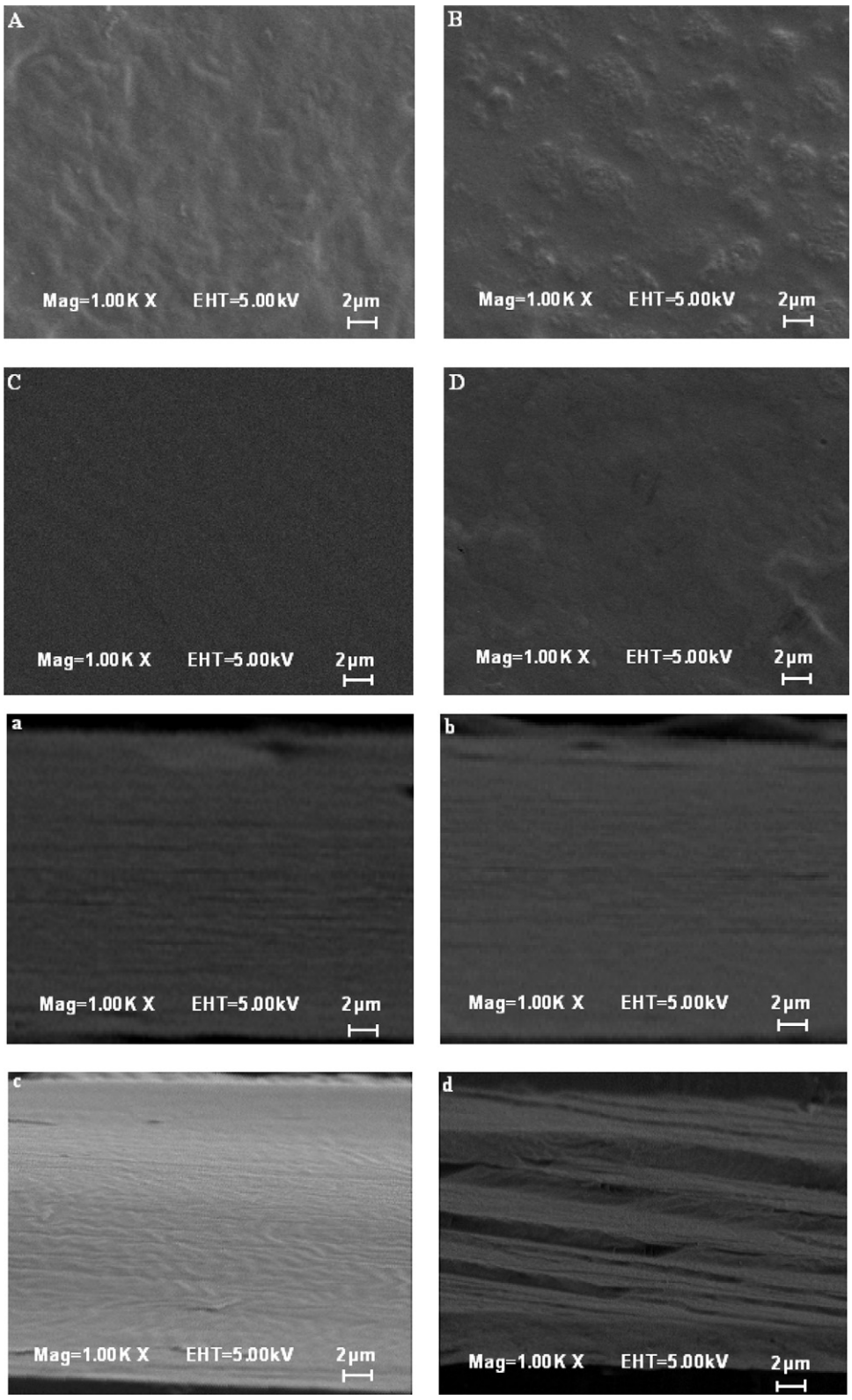

Fig. 2. SEM micrographs of the surface and cross-section of kudzu starch/ascorbic acid films. (A) Surface morphology of KA film, (B) surface morphology of KAS film, (C) surface morphology of KAT film, (D) surface morphology of KAST film; (a) cross-section morphology of KA film, (b) cross-section morphology of KAS film, (c) cross-section morphology of KAT film, and (d) cross-section morphology of KAST film.

of hydrocolloid substances (Phan The, Debeaufort, Voilley, & Luu, 2009). As seen from Fig. 2, KAT film had a more compact matrix (Fig. 2c); while the cross sections of KA and KAS films were similar, which presented slightly heterogeneous structures and few discontinuous zones (Fig. 2a and b). However, KAST film showed a folded structure in the cross-sectional view (Fig. 2d), similar results were obtained with films produced from tapioca starch/decolorized hsian-tsao leaf gum and sucrose ester surfactants (Chen et al., 2009). The internal morphology differences of the above films were probably due to the different properties of the surfactants. Tween

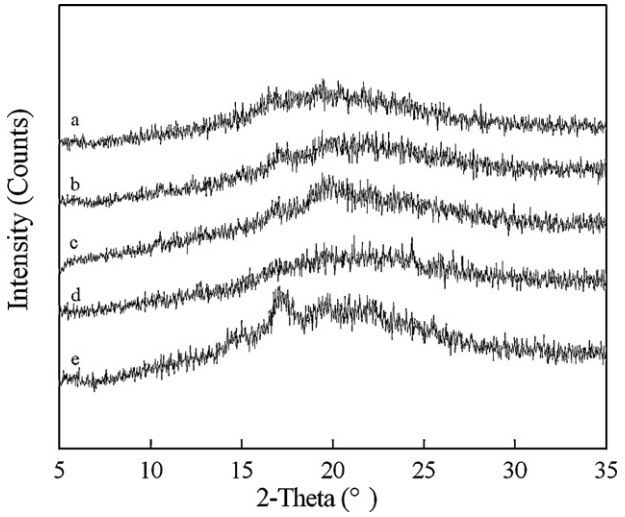

Fig. 3. X-ray diffraction patterns of kudzu starch film and kudzu starch/ascorbic acid films. (a) KA film, (b) KAS film, (c) KAT film, (d) KAST film, and (e) kudzu starch film.

20 could disperse in the film-forming solution and promote its flexibility, leading to more smooth structure of the resulted film. Span 80 was insoluble in water and tended to transfer to the surface of the film, making the internal structure of KAS film similar with that of KA film. As regard to the addition of the blended-surfactant, although tween 20 could promote the solubility of span 20, span 20 formed micelles in the solution which would aggregate during the drying process and then resulted in folded structure of the film (Chen et al., 2009).

3.5. X-ray diffraction

The X-ray diffractogram of the glycerol plasticized kudzu starch film showed a partially crystalline structure, with the peak at 17° and 20° implied the formation of double-helical B-type crystalline and the single helical crystal structure of V-type, respectively (Fig. 3).

The incorporation of ascorbic acid and surfactants into the films generally decreased the intensity of the characteristic peaks observed, indicating that the intermolecular interactions among the components limited the molecular chain segment movements and then restrained the crystallization processes of the films. However, the intensity of the peak at 20° for KAT film increased compared with native plasticized kudzu starch film. This change may be assigned to V-type crystal due to amylose–tween complexes (Mondragón et al., 2008). As for span 80 addition, the increased trend of the V-type crystal was not obvious. It was probably because of the poorer compatibility of span 80 molecules in kudzu starch systems which led to less available molecules for complexation (Lay Ma, Floros, & Ziegler, 2011).

3.6. Surface hydrophobicity and wettability

In order to evaluate the surface hydrophobicity of the film, contact angle between the film surface and a water droplet was determined. It was reported that water contact angle increased with the increasing of surface hydrophobicity (Kokoszka, Debeaufort, Hambleton, Lenart, & Voilley, 2010). The static contact angle values ranged from ca. 23.9° to ca. 44.8° in the present study (Table 3) and were significantly ($P < 0.05$) affected by surfactant types. The addition of hydrophobic span 80 resulted in higher resistance of KAS film to liquid water wetting, which was ascribed to its migration onto the film surface and subsequently, the improved surface hydrophobicity. Besides, adding tween 20 reduced the contact angle slightly. It was probably due to the humectant effect of this surfactant. Similar result was found in agar-based films (Phan The et al., 2009). However, when the blended-surfactant was added, the film became more hydrophilic. The reason may be that the distances among the molecules deceased after film-forming process, and the hydrophobic groups of surfactants were more likely to interact with each other, leaving hydrophilic groups to face out. Consequently, the resistance of the KAST film surface to liquid water reduced obviously ($P < 0.05$). It can be concluded that the resistance of the film surface to liquid water was not only influenced by the properties of each component but also by the intermolecular interactions.

3.7. Water content and water vapor permeability

It can be found in Table 3 that water content deceased slightly when span 80 was added to the films, and tween 20 led to slightly higher water content. Nevertheless, the differences were not obvious ($P > 0.05$) among all the films. Andreuccetti et al. (2011) reported that water content of the gelatin-based films prepared with lecithin decreased with the increasing surfactant addition, while different levels of the more hydrophilic yucca extract resulted in similar moisture content. Villalobos et al. (2006) found greater reduction of water content in hydroxypropyl methylcellulose film when the more polar surfactant was used. The above differences may be resulted from the different properties of film matrix and surfactants, the different amount of surfactants used and the varied interactions among the components.

The mean WVP ranged from 4.88 to 9.27×10^{-11} g m^{-1} s^{-1} Pa^{-1} which generally did not show significant differences ($P > 0.05$) except for KAST film. As water vapor transfer process depended on the simultaneous actions of water solubility and diffusivity in a polymeric matrix (Müller, Laurindo, & Yamashita, 2009; Ziani, Oses, Coma, & Maté, 2008), the higher WVP for KAST film can be explained by its higher water affinity (which can be seen from the lower contact angle of water droplet on KAST film) and more water migration through its more heterogeneous internal structure (as seen from SEM). Andreuccetti et al. (2011) reported that the water insoluble lecithin resulted in higher WVP, while the water soluble yucca extract led to lower WVP. Rodríguez et al. (2006) found increasing WVP as the concentration of tween 20 increased, but the addition of higher content of span 80 led to lower WVP. Chen et al. (2010) pointed out that it was a relatively new approach to improve the water barrier properties of a hydrophilic film by adding surfactant. Thus, we must analyze each case concretely when we study the water barrier properties of different films, even though they possess similar raw materials and film formulations.

3.8. Mechanical properties

Results of the tensile tests were shown in Table 3. The mean TS values varied from 5.46 to 13.70 MPa and EB values ranged from 36.60% to 53.92% depending on the dosage of surfactant. It was clear that the presence of surfactant caused slight decreases of tensile strength but increases of elongation, which meant that the surfactants behaved mechanically as plasticizers. Several previous studies showed the negative effects of surfactants on both of TS and EB values (Carneiro-da-Cunha, Cerqueira, Souza, Souza, Teixeira, & Vicente, 2009; Ziani et al., 2008). However, Rodríguez et al. (2006) reported that EB of glycerol plasticized potato starch film was increased with addition of higher amount of surfactant due to synergistic effects between glycerol and the surfactants, which was similar with our result.

3.9. Film solubility

The solubility of KA film was 36.9% (Table 3), which was in the same range of other starch based films (Bertuzzi, Armada, & Gottifredi, 2007). With addition of surfactants, film solubility increased. Compared with the KAS film, KAT film showed significantly ($P < 0.05$) higher solubility. Moreover, maximum solubility of 41.5% was observed with the blended-surfactant addition, but this value was comparable with that of KST film. The above phenomenon reflected the inherent hydrophilic properties of tween 20.

4. Conclusion

Surface tension of the kudzu starch/ascorbic acid film-forming solution decreased with the addition of surfactants. Tween 20 improved the wettability of film-forming solution on both glass and paraffin wax substrates whereas span 80 led to poorer wettability on glass substrates. Surfactants can delay the release of ascorbic acid into water due to their partly hydrophobic characters. The film surface morphologies were generally continuous and homogeneous except that KAS film showed small globules, but the cross-section morphologies were always different depending on different surfactants. The addition of ascorbic acid and surfactants decreased the crystal structures of kudzu starch films, but tween 20 promoted the formation of V-type crystal. KAT film presented higher flexibility, water content and solubility, lower mechanical strength and comparable water barrier ability as compared with KAS film. Moreover, KAST film had comparable wettability and mechanical properties but worse water barrier ability as regarding to the other two films.

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