



Relationships between the gelatinization of starches and the textural properties of extruded texturized soybean protein-starch systems



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ABSTRACT

Starches from diverse sources have different thermal properties and, thus, show different gelatinization degrees under a specific extrusion condition, which affects the quality of the extrudates. To find the appropriate ingredients for extruding texturized soybean protein-starch mixtures, the thermal properties of commercial-grade starches (wheat starch, corn starch, potato starch, sweet potato starch, cassava starch, mung bean starch, pea starch, amylose from potato, and amylopectin from waxy corn), blends of starches with soybean protein isolate (SPI) and wheat gluten were assessed. The extrusion response parameters (torque, pressure change, specific mechanical energy (SME), and on-line apparent viscosity) during extrusion and the thermal and textural properties of the extrudates were determined. Pearson correlation analysis showed that the enthalpy changes of the blends were directly correlated with the torque, pressure change, specific mechanical energy, and on-line apparent viscosity, whereas those parameters were inversely correlated with the fibrous degree of the extrudates. The hardness, tensile strength, lengthwise strength, and fibrous degree of the extrudates were correlated with the enthalpy changes of the blends. The springiness and fibrous degree of the extrudates were correlated with the half-peak height of the blends. It was concluded that a higher enthalpy changes of blends leads to a higher SME and a pressure change, which results in a higher hardness and tensile strength and a lower fibrous degree of the extrudates.

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1. Introduction

USA Food and Drug Administration claimed that “25 g of soy protein a day, as part of a diet low in saturated fat and cholesterol, may reduce the risk of heart disease” and also granted recognition for soy in 1999, which popularized the foods made from soy or soy protein, such as texturized soybean protein. Texturized soybean protein shows obvious fibrous structure and a remarkable similarity in appearance, texture and mouth feel to meat, so those textural properties are the key factors to consumer acceptance (Ranasinghesagara et al., 2005, 2006). The extruded defatted soybean meal has a remarkable fibrous structure comparing with SPI, which indicates that the fiber was affected by introducing carbohydrate into the protein phase (Sheard et al., 2007).

The essential effects of the extrusion process are due to high

shear and temperature. Thermo-mechanical action during extrusion cooking leads to the denaturation of proteins and the gelatinization of starches; these effects have been characterized by thermal properties of protein and starches (Alonso et al., 2000; Barron et al., 2002; Batterman-Azcona et al., 1999; Harper and Clark, 1979; Kitabatake et al., 1985; Liu et al., 2011; Zhang et al., 2001). Differential scanning calorimetry (DSC) has been used to study the enthalpy changes of the thermal denaturation of proteins and gelatinization of starches (Baeza and Pilosof, 2002; Boye and Alli, 2000; Galani and Apenten, 2000; Hendrix et al., 2000; Li et al., 2004a; Tufvesson et al., 2003; Yu and Christie, 2001). In the DSC curve of SPI, two peaks were observed at 90 °C and 109 °C, which probably correspond to the denaturation of the 7S and 11S, and the similar result was obtained at 80 °C and 95 °C (Li et al., 2014; Ortiz and Añón, 2001). One peak of acetic acid-soluble wheat gluten at 74 °C and two peaks of washed wheat gluten at 88 °C and 101 °C were observed (Eliasson and Hegg, 1980; Lawton and Wu, 1993). The gelatinization of various starches with different water content has been well studied. Starch thermal changes under

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limited water content had been well described by so-called Flory law, which described the relationship between the melting point of a crystalline polymer with dilute concentration (Donovan, 1979). A large gelatinization endotherm was found at approximately 70 °C for waxy and maize starch (Russell, 1987), and a second endotherm referring to the phase transition within an amylose–lipid complex was also detected for maize starch at approximately 90 °C (Jovanovich and Añón, 1999; Raphaelides and Karkalas, 1988). Meanwhile, there is an endotherm for waxy starch with 55% water content, which reflected the non-equilibrium melting of crystallites (Liu et al., 2006; Shogren, 1992).

Great interest has been given to the thermal properties of protein–starch mixtures. The thermal transition temperature of wheat-flour/potato-starch mixture with 30% moisture content increased from 62 to 66 °C and 64–66 °C separately, when the addition of two varieties potato starch increased from 10% to 50% (Zaidul et al., 2008). The peak temperatures of the starch gelatinization increased from 70 to 83 °C in a starch–gluten system with 60% moisture content, with the increasing addition of Hard Red Spring wheat protein extract from 5% to 50% (Mohamed and Rayas-Duarte, 2003). The starch gelatinization has a significant effect on the physical properties of the extruded products. The water solubility index of corn starch extrudate increased with the gelatinized corn starch content increasing, since only starch granules degraded beyond gelatinization could participate in the formation of a stable, expanded structure (Gomez and Aguilera, 1984). Asaoka et al. (2006) found that the bulk density decreased as gelatinization of the cassava starch increased, and the minimum bulk density occurred between 55% and 75% gelatinization.

Still there is insufficient research on enthalpy changes during the extrusion process, such as (1) how the thermal transition properties of proteins and starches change after mixing and extrusion, and (2) what is the relationship between the enthalpy changes of blends and textural properties of texturized soybean protein? The purpose of this research is to study the relationships among the enthalpy changes of the blends, extrusion response parameters, and textural properties of the extrudates. The results will help to select the ingredients and optimize the formula of extruded textured soybean protein–starch mixtures.

2. Materials and methods

2.1. Materials

Soybean protein isolate (Injected 5100) was purchased from Yuxin Group Ltd. (Shandong Province, China). The moisture content was 6.98%. The protein content was 94.44% (dry basis). Wheat gluten was purchased from Ruixiang Group Ltd. (Shandong Province, China). The moisture content was 7.21%. The protein content was 85.73% (dry basis). Wheat starch, corn starch, potato starch, sweet potato starch, cassava starch, mung bean starch, pea starch, potato amylose and corn amylopectin were acquired in a market. The total starch content of the starches from different botanical sources, measured according to Chinese standard method GB/T 5009.9-2003 by third-party inspection companies (Silliker, Shanghai), are specified in Table 1. Soybean protein isolates and wheat gluten were mixed with 9 different starches at a ratio of 65:15:20, respectively.

2.2. Extrusion

2.2.1. Extruder

All of the extrusion experiments were conducted using a pilot-scale, co-rotating and intermeshing twin-screw DSE-25 extruder (Brabender GmbH and Co., Germany). The screw profile from feed

Table 1

Total starch content of starches from different botanical sources.

Starch	Starch content (%. d.b) ^a	Moisture content (%)
Wheat starch	94.52 ± 0.00d	12.16% ± 0.15b
Corn starch	99.51 ± 0.00a	10.85% ± 0.16d
Potato starch	98.44 ± 0.74a	15.99% ± 0.03a
Sweet potato starch	99.23 ± 0.57a	11.55% ± 0.07c
Cassava starch	93.98 ± 0.02d	10.76% ± 0.02d
Mung bean starch	97.37 ± 0.42b	12.51% ± 0.59b
Pea starch	95.75 ± 0.55c	12.14% ± 0.08b
Potato amylose	98.66 ± 0.63a	12.05% ± 0.02b
Corn amylopectin	92.90 ± 0.31e	12.06% ± 0.01b

^a Means ± standard deviations; different letters mean significant differences ($P < 0.05$).

to the die is with CE/37.5/37.5/8 and CE/25/45/8, which represented 8 conveying elements with 37.5 mm length and 37.5° helix angle together with another 8 conveying elements with 25 mm length and 25° helix angle, respectively. The extruder parameters were 25 mm screw diameter (D); 20:1 screw length/diameter ratio; and $2 \times 20 \times 100$ mm cooling die attached to the end of the extruder. The barrel was segmented into a feeding zone and five temperature-controlled zones, which were heated by an electric cartridge heating system and cooled with running water. The temperature and screw speed were monitored from a control panel. The extruder responses, including the motor torque and die pressure, were recorded on-line once every 10 s automatically.

2.2.2. Extrusion conditions

The blends were fed into the extruder at a speed of 30 g min⁻¹ (dry basis). Based on preliminary experiments and the working stability of the extruder, the feed moisture content was selected as 50% (dry basis), the screw speed was 160 r min⁻¹, and the extruder barrel temperatures were kept at 60, 80, 145, 137 and 70 °C from the first zone to the fifth zone (die), respectively.

2.2.3. Specific mechanical energy

The specific mechanical energy (SME, kJ kg⁻¹) was calculated from the screw speed ($n = 160$ r min⁻¹), motor torque (T, N·m, recorded automatically by computer) and mass flow rate (MFR, g min⁻¹, determined by the output of the extrudate within 1 min), according to the following formula (Chen et al., 2010; Godavarti and Karwe, 1997):

$$SME = \frac{2\pi \times n \times T}{MFR}$$

2.2.4. On-line viscosity

The on-line viscosity at the die of each treatment was calculated according to the method described by Li et al. (2004b), using the equation below:

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{\Delta PH}{2L} \Big/ \frac{6V}{BH^2} = \frac{\Delta PBH^2}{12LV} = \frac{\Delta PBH^3}{12L(s \times B \times H)} = \frac{\Delta PH^2}{12Ls}$$

where η is the apparent viscosity (Pa·s); τ is the shear stress (Pa); $\dot{\gamma}$ is the shear rate (s⁻¹); ΔP is the die pressure drop (Pa); H , L , and B are the known geometries of the viscometer channel (mm); and s is the velocity of the extrudates coming out from the die (mm s⁻¹), which was measured according to the lengths of the extrudates within 2 min.

2.2.5. Sample collection

When the extruder reached a steady state, as indicated by the

constant values for the extruder motor torque and die pressure, three sets of samples were collected, cooled for five minutes and then immediately put into the airtight plastic bags and frozen at $-18\text{ }^{\circ}\text{C}$ for future analysis, which included the textural measurement and DSC measurement of the extrudates. The samples for DSC measurement were freeze-dried at 0.037 mbar for 24 h using a freeze drier (Christ Alpha 1–4 LSC, Marin Christ, Germany).

2.3. Thermal transition properties

The thermal characteristics of the ingredients, blends and freeze-dried extrudates were studied using a differential scanning calorimeter (DSC, Q-200, TA Instruments, America). The samples were mixed with sufficient water in a vial to give a 50% moisture paste, and the vial was then capped and stored at $4\text{ }^{\circ}\text{C}$ overnight. When the vial reached room temperature, approximately 10 mg of the moisture-equilibrated material was weighed in a hermetic aluminum TA pan using a precision balance ($\pm 0.01\text{ mg}$, Analytical Plus, Mettler Toledo) and heated at the rate of $10\text{ }^{\circ}\text{C min}^{-1}$ between $20\text{ }^{\circ}\text{C}$ and $130\text{ }^{\circ}\text{C}$ under an inert atmosphere (50 mL min^{-1} of dry N_2). The reference was a void aluminum TA pan. The onset temperature (T_o), peak temperature (T_p), enthalpy changes (ΔH) and width at half-peak height ($\Delta T_{1/2}$) were computed from the curves by Universal Analysis Program, Version 1.9 D (TA Instruments). The enthalpies were calculated on a dry basis. The subscripts i, b and e used in T_o , T_p and ΔH mean the initial, blend and extrudate, respectively.

2.4. Textural properties

The textural properties of the fresh extrudates include the hardness, springiness, tensile strength, lengthwise strength, crosswise strength and fibrous degree; these properties were measured with a TA.XT2 Texture Analyzer (Stable Micro Systems, UK). According to Fang et al. (2014), a square piece ($1.5 \times 1.5\text{ mm}$) that was cut from a fresh product strip was compressed using a P/35 probe (cylinder, $\varnothing 35\text{ mm}$) to 50% of its original thickness at a speed of 1 mm s^{-1} for 5 s, and the hardness and springiness were recorded. Hardness is defined as the maximum peak force during the first compression cycle (first bite) and has often been substituted by the term firmness. Springiness was defined as the %distance to a return to zero force during withdrawal of the probe after compression. A sample in that shape, shown in Fig. 1a, was pulled using an A/TG probe (rigs and clamps) at a speed of 0.5 mm s^{-1} until the strip was broken, and the tensile strength was recorded. A sample (Fig. 1b) was cut using an A/CKB probe (knife blade) to 75% of its original thickness at a speed of 1 mm s^{-1} along the vertical direction (lengthwise strength, F_V) and parallel (crosswise strength, F_L) to the direction of the extrudate outflow from the extruder. The fibrous degree of texturization was expressed by the ratio of the lengthwise strength to crosswise strength. All of the determinations were repeated 10 times and averaged (Kang, 2007; Noguchi, 1989).

2.5. Statistical analysis

One-way analysis of variance (ANOVA) and Pearson correlation coefficients (r) were performed using the PASW Statistics 18.0 software. The comparisons between treatments were evaluated using Duncan's test. The significance level was set to 95% for all of the data analysis.

3. Results and discussion

3.1. Thermal transition properties of the initial ingredients

The transition temperatures (onset, T_o ; peak, T_p), enthalpy

changes (ΔH) and width at half-peak height ($\Delta T_{1/2}$) of the initial ingredients are shown in Tables 2 and 3. The curve of the SPI in Fig. 2 shows that there was one peak between $80\text{ }^{\circ}\text{C}$ and $120\text{ }^{\circ}\text{C}$ and the ΔH was 0.72 J g^{-1} , which was so tiny that almost invisible. Wheat gluten has two peaks ($69.86\text{ }^{\circ}\text{C}$ and $88.28\text{ }^{\circ}\text{C}$) between $60\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$ in the curve.

Native SPI shows a DSC curve that is characterized by two endotherm peaks, which correspond to the denaturation of β -conglycinin (7S fraction) ($T_p: 79.9 \pm 0.3\text{ }^{\circ}\text{C}$) and glycinin (11S fraction) ($T_p: 95.5 \pm 0.4\text{ }^{\circ}\text{C}$) (Ortiz and Añón, 2001). In our study, the SPI was commercial grade and was probably denatured in the manufacturing process, which resulted in overlap of the endotherm peaks of the 7S and 11S fractions. According to Eliasson and Hegg (1980), water washed wheat gluten (63% water content) was heated from 35 to $115\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$, and there were 2 protein denaturation endotherm peaks ($T_p: 88.4 \pm 1.8\text{ }^{\circ}\text{C}$ and $101.4 \pm 1.6\text{ }^{\circ}\text{C}$) in the curve, which was similar to the two endotherm peaks ($T_p: 77.14 \pm 0.36\text{ }^{\circ}\text{C}$ and $96.17 \pm 0.03\text{ }^{\circ}\text{C}$) in our study.

There is a clear endothermic peak in the temperature region between $61\text{ }^{\circ}\text{C}$ and $92\text{ }^{\circ}\text{C}$ for different starches. A significant difference was observed among the varieties of starches. The T_{oi} , T_{pi} , ΔH_i , and $\Delta T_{1/2i}$ for the various starches ranged from 56.00 to $87.81\text{ }^{\circ}\text{C}$, from 61.25 to $92.76\text{ }^{\circ}\text{C}$, from 0.49 to 5.29 J g^{-1} and from 6.50 to $12.14\text{ }^{\circ}\text{C}$, respectively. The CV of ΔH_i , $\Delta T_{1/2i}$, T_{oi} , and T_{pi} for the various starches decreased by 57.93%, 22.75%, 17.49%, and 16.31%, respectively. Wheat starch showed the lowest gelatinization temperatures, while sweet potato starch showed the highest. Potato starch showed the highest ΔH , while the amylopectin showed the lowest. The $\Delta T_{1/2}$ of mung bean starch ($12.14\text{ }^{\circ}\text{C}$) was considerably higher than that of the other starches. The corn, sweet potato, and cassava starches showed the highest transition temperatures and the lowest ΔH .

3.2. Thermal transition properties of blends

The DSC profiles and thermal transition properties of the blends of soy and wheat gluten with various starches are shown in Fig. 3 and Table 4. There was one significant endothermic peak of up to $120\text{ }^{\circ}\text{C}$ in each curve of blends, whose T_{ob} was from 62 to $78\text{ }^{\circ}\text{C}$, which indicates that the denaturation of the soy protein or wheat gluten overlapped the gelatinization of the starches. With regard to the various starches that were the variables in the blends, the denaturation of the soy protein or wheat gluten was supposed to be similar and is not discussed with respect to the different soy-wheat blends, and the thermal transition properties of 9 types of starches were focused on and compared.

It was observed that there were significant changes in the thermal transition properties of the starches after mixing. The T_{ob} , T_{pb} , ΔH_b , and $\Delta T_{1/2b}$ of the various blends ranged from 62.58 to $78.72\text{ }^{\circ}\text{C}$, from 73.98 to $87.71\text{ }^{\circ}\text{C}$, from 1.24 to 2.42 J g^{-1} and from 7.77 to $26.26\text{ }^{\circ}\text{C}$, respectively. It was observed that after blending, the transition temperatures (T_{ob} , T_{pb}) of wheat starch, pea starch, potato amylose and corn amylopectin increased, while the transition temperatures (T_{ob} , T_{pb}) of potato starch, sweet potato starch, cassava starch and mung bean starch decreased, and the opposite tendencies were observed with the ΔH_b . Compared to the initial starches, the CVs (Coefficient of Variation) of the transition temperatures (T_o , T_p) and ΔH decreased after blending, which presented the ratio of Standard-Deviation and Mean-value, indicating the variability of starches, blends and extrudates. The $\Delta T_{1/2}$ of all of the starches increased after blending, except for corn amylopectin.

Li et al. (2014) investigated the thermal properties of the SPI/corn starch mixture and found that the starches and SPI are independent during heating, appearing to be simply the sum of corn starch gelatinization and SPI denaturation with different ratios. The

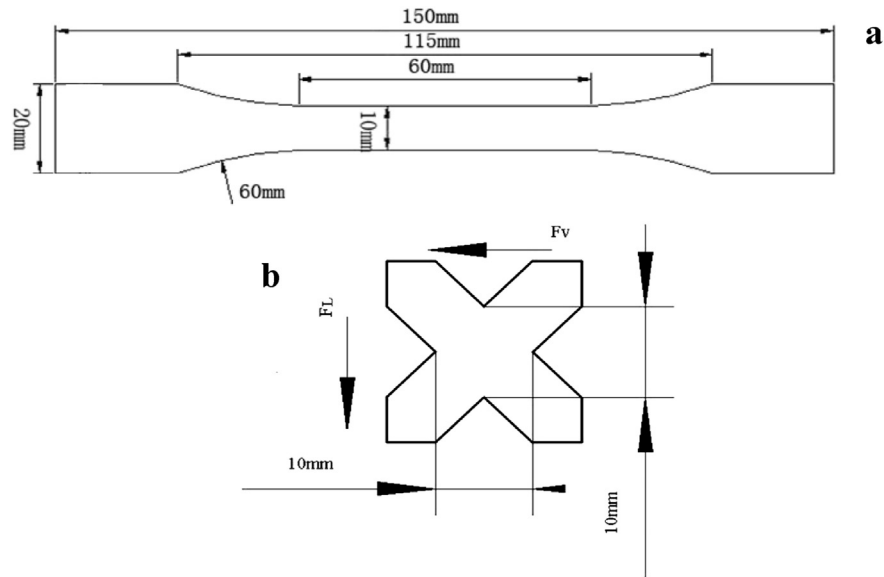


Fig. 1. Sampling sketch for tensile strength test (a) and fibrous degree test (b).

Table 2

Thermal transition properties of SPI and wheat gluten: onset (T_o), peak (T_p), enthalpy changes (ΔH) and the width at half-peak height ($\Delta T_{1/2}$)^a.

Ingredients	First endothermic peak				Second endothermic peak			
	T_{oi} (°C)	T_{pi} (°C)	ΔH_i (J·g ⁻¹)	$\Delta T_{1/2i}$ (°C)	T_{oi} (°C)	T_{pi} (°C)	ΔH_i (J·g ⁻¹)	$\Delta T_{1/2i}$ (°C)
SPI	88.62 ± 0.84	109.44 ± 6.81	0.72 ± 0.31	26.03 ± 3.12				
Wheat Gluten	69.86 ± 0.28	77.14 ± 0.36	0.90 ± 0.04	7.82 ± 0.47	88.28 ± 0.71	96.17 ± 0.03	0.31 ± 0.01	10.30 ± 0.19

^a Means ± standard deviations.

Table 3

Thermal transition properties of the starches: onset (T_o), peak (T_p), enthalpy changes (ΔH) and the width at half-peak height ($\Delta T_{1/2}$)^a.

Ingredients	T_{oi} (°C)	T_{pi} (°C)	ΔH_i (J·g ⁻¹)	$\Delta T_{1/2i}$ (°C)
Wheat starch	56.00 ± 0.33g	61.25 ± 0.37f	3.51 ± 0.07bc	6.56 ± 0.30b
Corn starch	83.62 ± 0.57b	89.12 ± 0.02b	1.08 ± 0.34fg	7.20 ± 0.40b
Potato starch	77.34 ± 1.46d	83.16 ± 0.82c	2.32 ± 0.80de	6.90 ± 0.93b
Sweet potato starch	87.81 ± 0.55a	92.76 ± 0.19a	0.49 ± 0.30g	6.98 ± 1.10b
Cassava starch	85.78 ± 1.23ab	90.62 ± 0.80b	1.74 ± 0.42ef	7.20 ± 0.01b
Mung bean starch	80.00 ± 1.78c	89.40 ± 1.82b	2.15 ± 0.15def	12.14 ± 0.65a
Pea starch	58.39 ± 0.75f	64.60 ± 0.33e	3.09 ± 0.93cd	6.50 ± 0.78b
Potato amylose	62.71 ± 0.83e	67.93 ± 0.61d	4.36 ± 0.46ab	7.42 ± 0.19b
Corn amylopectin	62.00 ± 0.05e	68.13 ± 0.03d	5.29 ± 0.16a	8.04 ± 0.15b
Average	72.63	78.55	2.67	7.66
CV (%)	17.49	16.31	57.93	22.75

^a Means ± standard deviations; different letters in the same column mean significant differences ($P < 0.05$).

shift in the T_p and the decrease in ΔH could be explained by the migration of water from the starch to the proteins (soy and wheat gluten) (Eliasson, 1983). With regard to that explanation, Mohamed and Rayas-Duarte (2003) observed that the T_o and T_p of wheat starch-gluten system increased because of the presence of wheat proteins: higher amounts of wheat protein (5–50%) decreased the ΔH of the wheat starch-gluten system from approximately 12 to 9 J g⁻¹.

3.3. Effect of the extrusion process on the thermal transition properties of the blends

The DSC profiles of the extrudates with various starches are shown in Fig. 4. The T_{oe} , T_{pe} , ΔH_e and $\Delta T_{1/2e}$ of the extrudates with different starches and the differences between the blends are shown in Table 5. A significant difference was observed among T_{pe} ,

ΔH_e and $\Delta T_{1/2e}$. The T_{oe} , T_{pe} , ΔH_e , and $\Delta T_{1/2e}$ of the extrudates varied from 42.93 to 47.28 °C, from 51.97 to 59.66 °C, from 0.67 to 1.97 J g⁻¹, and from 9.43 to 19.45 °C, respectively. Compared with the values of the blends, the thermal transition properties (T_o , T_p and ΔH) of the extrudates decreased.

After extrusion, the thermal properties (T_o , T_p and ΔH) of the extruded starches were significantly lower than those of native starches. Ozcan and Jackson (2005) found that after regular corn starch extrusion at a high temperature (165 °C), low moisture content (8.72%), and moderate shear (140 r min⁻¹), the starch will both gelatinize and melt into a fully cooked amorphous product; there was no DSC endotherm peak observed for the extruded starch because the starch crystallites are already melted/gelatinized in the extrusion process. Li et al. (2011) investigated the thermal properties of native corn starches and extruded starch films and found that there were endothermic peaks for the extruded films;

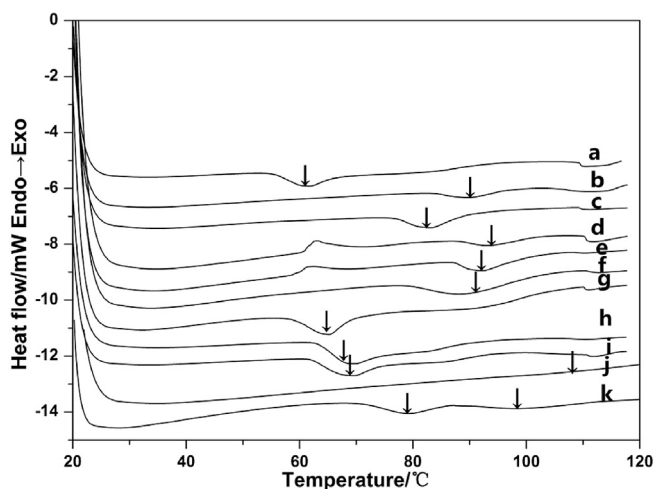


Fig. 2. DSC endotherms of (a) wheat starch; (b) corn starch; (c) potato starch; (d) sweet potato starch; (e) cassava starch; (f) mung bean starch; (g) pea starch; (h) potato amylose; (i) corn amylopectin; (j) SPI; (k) wheat gluten. The moisture content was 50%, and the heating rate was $10\text{ }^{\circ}\text{C min}^{-1}$.

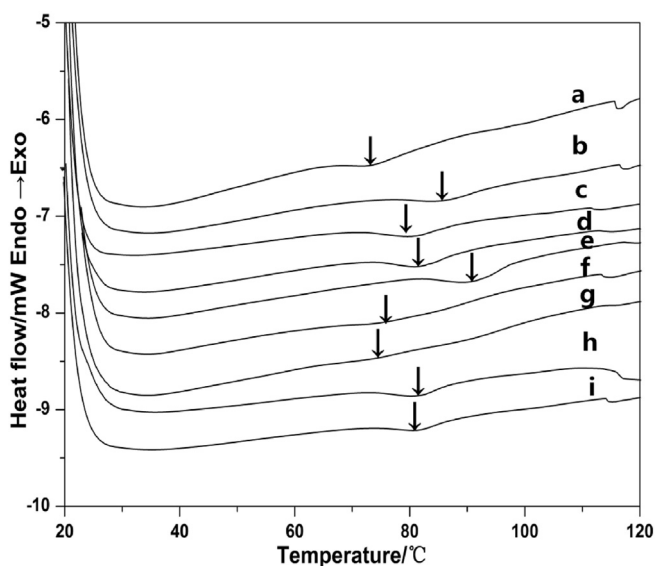


Fig. 3. DSC profiles of the blends with various starches: (a) wheat starch; (b) corn starch; (c) potato starch; (d) sweet potato starch; (e) cassava starch; (f) mung bean starch; (g) pea starch; (h) potato amylose; (i) corn amylopectin. The moisture content was 50%, and the heating rate was $10\text{ }^{\circ}\text{C min}^{-1}$.

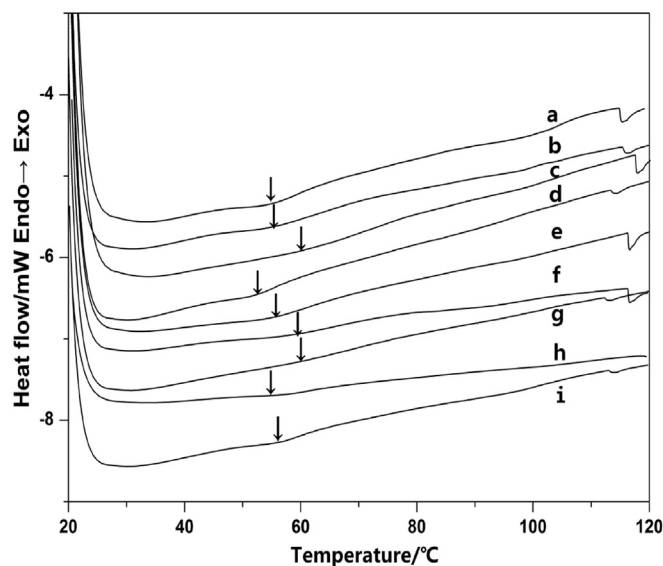


Fig. 4. DSC profiles of SPI: wheat gluten extrudates with various starches: (a) wheat starch; (b) corn starch; (c) potato starch; (d) sweet potato starch; (e) cassava starch; (f) mung bean starch; (g) pea starch; (h) potato amylose; (i) corn amylopectin. The moisture content was 50%, and the heating rate was $10\text{ }^{\circ}\text{C min}^{-1}$.

however, the values of T_0 , T_p and ΔH were significantly lower than those of gelatinization for those native starches, for example, a 66%–76% reduction in the ΔH value.

3.4. Effect of the enthalpy changes of the blends on the extrusion response parameters

Extrusion response parameters such as the torque, pressure change (ΔP), specific mechanical energy (SME) and on-line apparent viscosity (η) of the blends during extrusion are shown in Table 6. The torque, ΔP , SME and η varied from 18.80 to 36.22 N m, from 9.84 to 22.40 bar, from 308.70 to 633.61 kJ kg^{-1} and from 344.52 to 563.17 Pa s, respectively.

The correlation analysis between the extrusion response parameters and the enthalpy changes of the blends is provided. The ΔH values of the blends were significantly positively correlated with the torque ($r = 0.721$, $P < 0.05$), ΔP ($r = 0.777$, $P < 0.05$), SME ($r = 0.733$, $P < 0.05$) and η ($r = 0.875$, $P < 0.01$), which indicates that the thermal properties (mainly ΔH) of the blends could have a positive impact on the system parameters (torque, ΔP , SME and η) during extrusion. The relationship model obtained by quadratic

Table 4

Thermal transition properties of SPI: wheat gluten: starch (65:15:20) blends and difference between ingredients.

SPI: wheat gluten: starch blends	$T_{ob} (^{\circ}\text{C})$	$T_{pb} (^{\circ}\text{C})$	$\Delta H_b (\text{J} \cdot \text{g}^{-1})$	$\Delta T_{1/2b} (^{\circ}\text{C})$	$T_{ob} - T_{oi} (^{\circ}\text{C})$	$T_{pb} - T_{pi} (^{\circ}\text{C})$	$\Delta H_b - \Delta H_i (\text{J} \cdot \text{g}^{-1})$	$\Delta T_{1/2b} - \Delta T_{1/2i} (^{\circ}\text{C})$
Wheat starch	$66.47 \pm 0.93\text{cd}$	$73.98 \pm 0.52\text{d}$	$1.46 \pm 0.12\text{bc}$	$10.79 \pm 0.01\text{cd}$	10.47	12.73	-2.05	4.23
Corn starch	$74.90 \pm 0.13\text{b}$	$84.72 \pm 0.52\text{ab}$	$2.18 \pm 0.10\text{a}$	$11.91 \pm 0.33\text{c}$	-8.72	-4.40	1.10	4.71
Potato starch	$69.07 \pm 2.93\text{c}$	$77.93 \pm 3.93\text{c}$	$2.42 \pm 0.45\text{a}$	$9.72 \pm 1.58\text{cd}$	-8.27	-5.23	0.10	2.82
Sweet potato starch	$74.02 \pm 2.17\text{b}$	$82.42 \pm 1.44\text{b}$	$2.07 \pm 0.61\text{ab}$	$10.30 \pm 0.01\text{cd}$	-13.79	-10.34	1.58	3.32
Cassava starch	$78.72 \pm 0.04\text{a}$	$87.71 \pm 0.59\text{a}$	$2.22 \pm 0.05\text{a}$	$9.50 \pm 1.22\text{cd}$	-7.06	-2.91	0.48	2.30
Mung bean starch	$62.58 \pm 0.68\text{e}$	$75.89 \pm 0.02\text{cd}$	$2.32 \pm 0.13\text{a}$	$22.68 \pm 2.29\text{b}$	-17.42	-13.51	0.17	10.54
Pea starch	$64.14 \pm 1.05\text{de}$	$75.42 \pm 0.13\text{cd}$	$1.79 \pm 0.17\text{abc}$	$26.26 \pm 0.97\text{a}$	5.75	10.82	-1.30	19.76
Potato amylose	$72.84 \pm 0.61\text{b}$	$82.73 \pm 1.56\text{b}$	$2.17 \pm 0.17\text{a}$	$10.65 \pm 2.14\text{cd}$	10.13	14.80	-2.19	3.23
Corn amylopectin	$74.75 \pm 0.64\text{b}$	$81.67 \pm 0.78\text{b}$	$1.24 \pm 0.04\text{c}$	$7.77 \pm 0.55\text{d}$	12.75	13.54	-4.05	-0.27
Average	70.83	80.27	1.99	13.29	-1.80	1.72	-0.68	5.63
CV (%)	7.79	5.84	20.34	48.92	-9.71	-10.48	-37.59	26.18

^aMeans \pm standard deviations; different letters in the same column mean significant differences ($P < 0.05$); onset (T_0), peak (T_p), enthalpy changes (ΔH) and the width at half-peak height ($\Delta T_{1/2}$), subscripts i: initial and b: blend.

Table 5
Thermal transition properties of SPI: wheat gluten extrudates with different starches and difference between blends^a.

Extrudates	T _{oe} (°C)	T _{pe} (°C)	ΔH _e (J·g ⁻¹)	ΔT _{1/2e} (°C)	T _{oe} -T _{ob} (°C)	T _{pe} -T _{pb} (°C)	ΔH _e -ΔH _b (J·g ⁻¹)	ΔT _{1/2e} -ΔT _{1/2b} (°C)
Wheat starch	47.28 ± 2.33a	55.16 ± 0.69c	0.67 ± 0.53b	9.43 ± 2.35d	-19.19	-18.82	-0.79	-1.36
Corn starch	44.22 ± 1.87a	55.83 ± 0.11c	1.37 ± 0.04ab	13.84 ± 0.59bc	-30.68	-28.89	-0.81	1.93
Potato starch	45.74 ± 4.46a	59.66 ± 0.11a	1.21 ± 0.39b	19.45 ± 3.42a	-23.33	-18.27	-1.21	9.73
Sweet potato starch	43.02 ± 0.95a	51.97 ± 0.25e	0.87 ± 0.11b	10.16 ± 1.81cd	-31.00	-30.45	-1.20	-0.14
Cassava starch	42.93 ± 2.64a	55.27 ± 0.55c	1.97 ± 0.00a	15.15 ± 1.05b	-35.79	-32.44	-0.25	5.65
Mung bean starch	46.96 ± 1.58a	58.24 ± 0.14b	0.76 ± 0.41b	15.17 ± 0.81b	-15.62	-17.65	-1.56	-7.51
Pea starch	43.55 ± 1.71a	58.84 ± 0.80ab	1.06 ± 0.26b	17.68 ± 1.10ab	-20.59	-16.58	-0.73	-8.58
Potato amylose	44.25 ± 0.42a	53.82 ± 0.82d	1.03 ± 0.18b	10.11 ± 0.12cd	-28.59	-28.91	-1.14	-0.54
Corn amylopectin	46.84 ± 2.21a	56.12 ± 0.54c	0.95 ± 0.27b	10.14 ± 2.06cd	-27.91	-25.55	-0.29	2.37
Average	44.98	56.10	1.10	13.46	-25.86	-24.17	-0.89	0.17
CV (%)	3.89	4.40	35.60	27.42	-3.90	-1.44	15.26	-21.50

^a Means ± standard deviations; different letters in the same column mean significant differences ($P < 0.05$); onset (T_o), peak (T_p), enthalpy changes (ΔH) and the width at half-peak height (ΔT_{1/2}), subscripts e: extruded and b: blend.

Table 6
Response parameters for the extrusion of SPI: wheat gluten blends with different starches.

Extrusion response parameters	Torque(N·m)	ΔP(bar)	SME(kJ·kg ⁻¹)	η(Pa·s)
Wheat starch	28.10 ± 0.13g	15.31 ± 0.90f	463.84 ± 13.38f	429.26 ± 25.18e
Corn starch	32.76 ± 0.15d	18.27 ± 0.98e	532.15 ± 17.08c	523.23 ± 28.02d
Potato starch	31.28 ± 0.14f	20.99 ± 1.37c	504.74 ± 20.87e	633.61 ± 41.42a
Sweet potato starch	34.04 ± 0.14c	20.94 ± 0.83c	537.36 ± 15.51c	604.16 ± 23.85b
Cassava starch	32.78 ± 0.15e	19.07 ± 0.98d	523.97 ± 19.10d	578.00 ± 29.83c
Mung bean starch	34.64 ± 0.13b	21.56 ± 0.66b	545.15 ± 12.07b	596.11 ± 18.17b
Pea starch	36.22 ± 0.18a	22.40 ± 1.08a	563.17 ± 18.07a	597.26 ± 28.68b
Potato amylose	31.95 ± 0.14e	18.76 ± 0.82d	504.66 ± 14.11e	580.68 ± 25.55c
Corn amylopectin	18.80 ± 0.13h	9.84 ± 0.84g	344.52 ± 29.55g	308.70 ± 26.47f

*Means ± standard deviations; different letters in the same column mean significant differences ($P < 0.05$).

regression analysis was shown in Fig. 5, and the R² were 0.895 and 0.870, respectively.

The ΔH value reflects the amount of crystallinity in the starch structure (Liu et al., 2011). Under extrusion process, the starch crystalline structure of various blends was not disappeared completely, therefore the ΔH of extrudates still existed. In extruder barrel, the crystalline regions can act as “rigid structures” and have greater friction on the screws, which results in a higher torque and SME during the extrusion process. The higher the ΔH is, the more crystalline the material, which leads to the melt inside the cooling die becoming more viscous; therefore, the ΔP increases (Lin and Huff, 2000; Noguchi, 1989).

3.5. Effect of the extrusion response parameters on the textural properties of the extrudates

The textural properties of extrudates that have different starches are shown in Table 7. A significant difference was observed in the hardness, springiness, tensile strength, lengthwise strength, crosswise strength and fibrous degree. The hardness, springiness,

tensile strength, lengthwise strength, crosswise strength and fibrous degree ranged from 9.53 to 14.07 kg, from 0.83 to 0.93, from 0.27 to 0.45 kg, from 0.70 to 1.11 kg, from 0.97 to 1.37 kg, and from 1.12 to 1.40, respectively.

The correlation analysis between the extrusion response parameters and the textural properties of the extrudates was obtained. The torque was significantly positively correlated with the springiness ($r = 0.897$, $P < 0.01$), tensile strength ($r = 0.741$, $P < 0.05$) and lengthwise strength ($r = 0.787$, $P < 0.05$) of the extrudates, while it was significantly negatively correlated with the fibrous degree ($r = -0.928$, $P < 0.01$). ΔP and SME were significantly positively correlated with the springiness ($r = 0.824$, 0.891 , $P < 0.01$), tensile strength ($r = 0.751$, 0.747 , $P < 0.05$) and lengthwise strength ($r = 0.815$, 0.811 , $P < 0.01$) and negatively correlated with the fibrous degree ($r = -0.929$, -0.926 , $P < 0.01$). The η of the blends was significantly positively correlated with the hardness ($r = 0.702$, $P < 0.05$), springiness ($r = 0.699$, $P < 0.01$), tensile strength ($r = 0.793$, $P < 0.05$) and lengthwise strength ($r = 0.883$, $P < 0.01$) and negatively correlated with the fibrous degree ($r = -0.842$, $P < 0.01$). The relationship model of SME and the

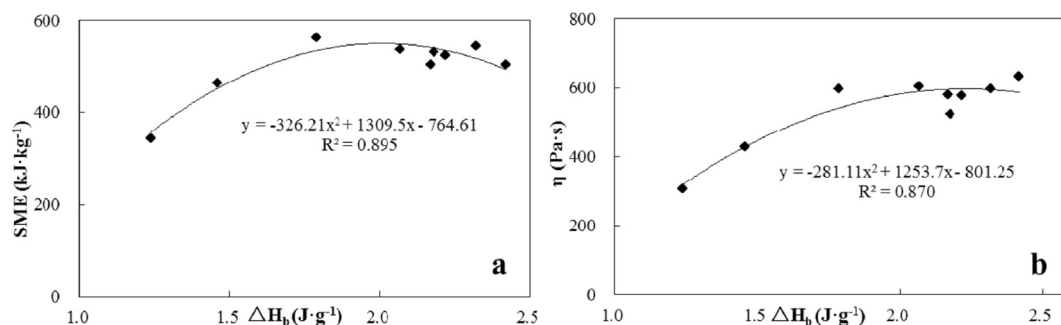


Fig. 5. The relationship between the enthalpy changes of the blends and the extrusion response parameters (a: SME, b: η).

Table 7
Textural properties of SPI: wheat gluten extrudates with different starches.

SPI: wheat gluten: starch extrudates	Hardness(kg)	Springiness	Tensile strength (kg)	Lengthwise strength(kg)	Crosswise strength(kg)	Fibrous degree
Wheat starch	11.26 ± 1.63bc	0.86 ± 0.04c	0.33 ± 0.08d	0.84 ± 0.03f	1.10 ± 0.04d	1.31 ± 0.07ab
Corn starch	12.95 ± 2.17ab	0.89 ± 0.02bc	0.45 ± 0.06a	0.98 ± 0.05cde	1.11 ± 0.10d	1.15 ± 0.15cde
Potato starch	14.07 ± 2.09a	0.86 ± 0.09cd	0.44 ± 0.08ab	1.05 ± 0.05b	1.23 ± 0.08b	1.18 ± 0.10cde
Sweet potato starch	12.23 ± 2.07ab	0.89 ± 0.02bc	0.39 ± 0.06abcd	1.02 ± 0.03bc	1.20 ± 0.07bc	1.18 ± 0.07cde
Cassava starch	12.22 ± 2.18ab	0.89 ± 0.01bc	0.36 ± 0.07cd	1.11 ± 0.07a	1.37 ± 0.07a	1.24 ± 0.08bc
Mung bean starch	12.01 ± 2.36ab	0.91 ± 0.01ab	0.43 ± 0.03abc	0.99 ± 0.09cd	1.09 ± 0.10d	1.12 ± 0.18de
Pea starch	11.24 ± 4.15bc	0.93 ± 0.01a	0.37 ± 0.10bcd	0.94 ± 0.05de	1.02 ± 0.07e	1.09 ± 0.12e
Potato amylose	10.91 ± 1.22bc	0.88 ± 0.02bc	0.42 ± 0.07abc	0.93 ± 0.05e	1.13 ± 0.08cd	1.23 ± 0.09bcd
Corn amylopectin	9.53 ± 1.09c	0.83 ± 0.02d	0.27 ± 0.03e	0.70 ± 0.02g	0.97 ± 0.06e	1.40 ± 0.09a

*Means ± standard deviations; different letters in the same column mean significant differences ($P < 0.05$).

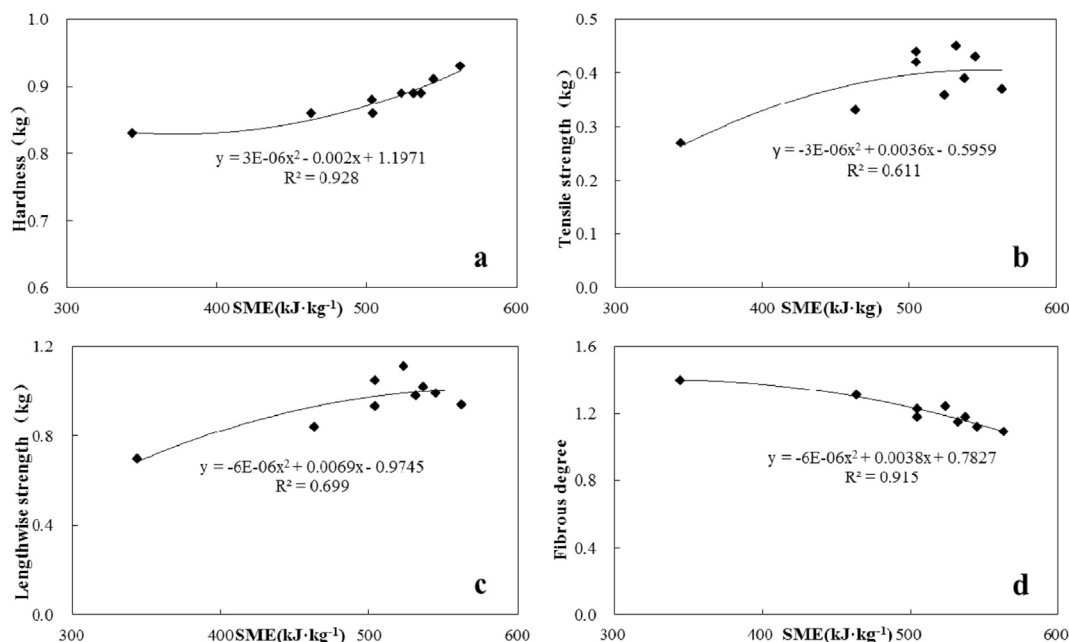


Fig. 6. The relationship between SME and the textural properties of extrudates (a: Hardness, b: Tensile strength, c: Lengthwise strength, d: Fibrous degree).

textural properties was shown in Fig. 6, and the R^2 were 0.928, 0.611, 0.699 and 0.915, respectively.

Chen et al. (2010) found that SME was positively correlated with the tensile strength ($r = 0.96$, $P < 0.01$), hardness ($r = 0.76$, $P < 0.01$), and chewiness ($r = 0.74$, $P < 0.01$) of the extrudates but negatively correlated with the fibrous degree ($r = -0.49$). On this basis, Fang et al. (2014) found that a higher SME resulted in extrudates that had a higher tensile strength and hardness, and an increased SME appeared to cause a decrease in the texturization degree. These results were generally consistent with our results.

3.6. The relationship between the enthalpy changes of the blends and the textural properties of the extrudates

Several significant correlations were observed between the enthalpy changes of the blends and the textural properties and extrudates. The ΔH_b was positively correlated with the hardness, tensile strength, and lengthwise strength and negatively correlated with the fibrous degree ($r = 0.797$, 0.896 , 0.888 and -0.693 , respectively). The $\Delta T_{1/2}$ value was positively correlated with the springiness and negatively correlated with the fibrous degree ($r = 0.813$ and -0.711 , respectively).

The effect of the thermal properties of the raw material on the textural properties of the extrudates should be interpreted in terms

of the impact of the enthalpy changes of the raw material on SME and η and the relationship between the extrusion response parameters (SME and η) and textural properties of the extrudates. The results indicated that the thermal properties (mainly enthalpy changes) can affect the textural properties of the extrudates by influencing the extrusion response parameters (SME and η) during extrusion.

4. Conclusions

During the extrusion, the transition temperatures and the enthalpy of all of the starches decreased, indicating a certain degree of cooking. At the same time, a higher ΔH of the blends led to a lower fibrous degree but a higher tensile strength and hardness of extruded texturized soybean protein. This finding occurred because the ΔH values of the blends were significantly positively correlated with the torque, ΔP and SME of the extrusion and a higher ΔP or torque during extrusion.

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References

- Alonso, R., Orúe, E., Zabalza, M.J., Grant, G., Marzo, F., 2000. Effect of extrusion cooking on structure and functional properties of pea and kidney bean proteins. *J. Sci. Food Agric.* 80 (3), 397–403.
- Asaoka, M., Blanshard, J.M.V., Rickard, J.E., 2006. Seasonal effects on the physicochemical properties of starch from four cultivars of cassava. *Starch Stärke* 43 (12), 455–459.
- Baeza, R.I., Pilosof, A.M.R., 2002. Calorimetric studies of thermal denaturation of β -lactoglobulin in the presence of polysaccharides. *LWT-Food Sci. Technol.* 35 (5), 393–399.
- Barron, C., Della Valle, G., Colonna, P., Vergnes, B., 2002. Energy balance of low hydrated starches transition under shear. *J. Food Sci.* 67 (4), 1426–1437.
- Batterman-Azcona, S.J., Lawton, J.W., Hamaker, B.R., 1999. Microstructural changes in zein proteins during extrusion. *Scanning* 21 (3), 212–216.
- Boye, J.I., Alli, I., 2000. Thermal denaturation of mixtures of α -lactalbumin and β -lactoglobulin: a differential scanning calorimetric study. *Food Res. Int.* 33 (8), 673–682.
- Chen, F.L., Wei, Y.M., Zhang, B., Ojokoh, A.O., 2010. System parameters and product properties response of soybean protein extruded at wide moisture range. *J. Food Eng.* 96 (2), 208–213.
- Donovan, J.W., 1979. Phase transitions of the starch-water system. *Biopolymers* 18, 263–275.
- Eliasson, A.C., 1983. Differential scanning calorimetry studies on wheat starch-gluten mixtures: I. Effect of gluten on the gelatinization of wheat starch. *J. Cereal Sci.* 1 (3), 199–205.
- Eliasson, A.C., Hegg, P.O., 1980. Thermal stability of wheat gluten. *Cereal Chem.* 57 (6), 436–437.
- Fang, Y.Q., Zhang, B., Wei, Y.M., 2014. Effects of the specific mechanical energy on the physicochemical properties of texturized soy protein during high-moisture extrusion cooking. *J. Food Eng.* 121, 32–38.
- Galani, D., Apenten, R.K.O., 2000. Revised equilibrium thermodynamic parameters for thermal denaturation of β -lactoglobulin at pH 2.6. *Thermochim. Acta* 363 (6), 137–142.
- Godavarti, S., Karwe, M.V., 1997. Determination of specific mechanical energy distribution on a twin-screw extruder. *J. Agric. Eng. Res.* 67 (4), 277–287.
- Gomez, M.H., Aguilera, J.M., 1984. A physicochemical model for extrusion of corn starch. *J. Food Sci.* 49 (1), 40–43.
- Harper, J.M., Clark, J.P., 1979. Food extrusion. *Crit. Rev. Food Sci. Nutr.* 11 (2), 155–215.
- Hendrix, T., Griko, Y.V., Privalov, P.L., 2000. A calorimetric study of the influence of calcium on the stability of bovine α -lactalbumin. *Biophys. Chem.* 84 (1), 27–34.
- Jovanovich, G., Anón, M.C., 1999. Amylose-lipid complex dissociation. A study of the kinetic parameters. *Biopolymers* 49 (1), 81–89.
- Kang, L.N., 2007. Texturization Technology and Mechanism of Soy Protein by High Moisture Extrusion, College of Food Science and Engineering, Northwest Agriculture and Forestry University, Yangling China.
- Kitabatake, N., Megard, D., Cheftel, J.C., 1985. Continuous gel formation by HTST extrusion-cooking: soy proteins. *J. Food Sci.* 50 (5), 1260–1265.
- Lawton, J.W., Wu, Y.V., 1993. Thermal behavior of annealed acetic acid-soluble wheat gluten. *Cereal Chem.* 70, 471–471.
- Li, M., Liu, P., Zou, W., Yu, L., Xie, F.W., Pu, H.Y., Liu, H.S., Chen, L., 2011. Extrusion processing and characterization of edible starch films with different amylose contents. *J. Food Eng.* 106 (1), 95–101.
- Li, M.S., Klimov, D.K., Thirumalai, D., 2004a. Thermal denaturation and folding rates of single domain proteins: size matters. *Polymer* 45 (2), 573–579.
- Li, P.X., Campanella, O.H., Hardacre, A.K., 2004b. Using an in-line slit-die viscometer to study the effects of extrusion parameters on corn melt rheology. *Cereal Chem.* 81 (1), 70–76.
- Li, S.J., Wei, Y.M., Fang, Y.Q., Zhang, W., Zhang, B., 2014. DSC study on the thermal properties of soybean protein isolates/corn starch mixture. *J. Therm. Anal. Calorim.* 115 (2), 1633–1638.
- Lin, S., Huff, H.E., 2000. Texture and chemical characteristics of soy protein meat analog extruded at high moisture. *J. Food Sci.* 65 (2), 264–269.
- Liu, H.S., Yu, L., Xie, F.W., Chen, L., 2006. Gelatinization of cornstarch with different amylose/amylopectin content. *Carbohydr. Polym.* 65 (3), 357–363.
- Liu, P., Xie, F.W., Li, M., Liu, X.X., Yu, L., Halley, P.J., Chen, L., 2011. Phase transitions of maize starches with different amylose contents in glycerol–water systems. *Carbohydr. Polym.* 85 (1), 180–187.
- Mohamed, A.A., Rayas-Duarte, P., 2003. The effect of mixing and wheat protein/gluten on the gelatinization of wheat starch. *Food Chem.* 81 (4), 533–545.
- Noguchi, A., 1989. Extrusion cooking of high-moisture protein foods. In: Mercier, C., Linko, P., Harper, J.M. (Eds.), *Extrusion Cooking*.
- Ortiz, S.E.M., Anón, M.C., 2001. Enzymatic hydrolysis of soy protein isolates. DSC study. *J. Therm. Anal. Calorim.* 66 (2), 489–499.
- Ozcan, S., Jackson, D.S., 2005. Functionality behavior of raw and extruded corn starch mixtures. *Cereal Chem.* 82 (2), 223–227.
- Ranasinghesagara, J., Hsieh, F., Yao, G., 2005. An image processing method for quantifying fiber formation in meat analogs under high moisture extrusion. *J. Food Sci.* 70 (8), E450–E454.
- Ranasinghesagara, J., Hsieh, F., Yao, G., 2006. A photon migration method for characterizing fiber formation in meat analogs. *J. Food Sci.* 71 (5), E227–E231.
- Raphaelides, S., Karkalas, J., 1988. Thermal dissociation of amylose-fatty acid complexes. *Carbohydr. Res.* 172 (1), 65–82.
- Russell, P.L., 1987. Gelatinisation of starches of different amylose/amylopectin content. A study by differential scanning calorimetry. *J. Cereal Sci.* 6 (87), 133–145.
- Sheard, P.R., Fellows, A., Ledward, D.A., Mitchell, J.R., 2007. Macromolecular changes associated with the heat treatment of soya isolate. *Int. J. Food Sci. Technol.* 21 (1), 55–60.
- Shogren, R.L., 1992. Effect of moisture content on the melting and subsequent physical aging of cornstarch. *Carbohydr. Polym.* 19 (2), 83–90.
- Tufvesson, F., Wahlgren, M., Eliasson, A.C., 2003. Formation of amylose-lipid complexes and effects of temperature treatment. Part 1. Monoglycerides. *Starch Stärke* 55 (2), 61–71.
- Yu, L., Christie, G., 2001. Measurement of starch thermal transitions using differential scanning calorimetry. *Carbohydr. Polym.* 46 (2), 179–184.
- Zaidul, I.S.M., Yamauchi, H., Matsuura-Endo, C., Takigawa, S., Noda, T., 2008. Thermal analysis of mixtures of wheat flour and potato starches. *Food Hydrocoll.* 22 (4), 499–504.
- Zhang, J., Mungara, P., Jane, J., 2001. Mechanical and thermal properties of extruded soy protein sheets. *Polymer* 42, 2569–2578.