Effect of Extrusion Treatment on Rheological Properties and *in Vitro* Digestibility of Pea Starch

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Abstract: This study investigated the influence of different extrusion conditions including pea starch moisture content (25%, 35%, 40%, 45% and 55%), barrel temperature (50, 60, 70, 80 and 90 ℃) and screw speed (100, 120, 140, 160 and 180 r/min) on the *in vitro* starch digestibility and rheological properties of pea starch. Hydrolysis degree (HD) was measured using an *in vitro* digestion model, and rheological properties were determined through steady shear test, frequency sweep test and temperature sweep test. The results showed that after extrusion treatment, HD and the relative content of slowly digestible starch (SDS) increased whereas the relative content of resistant starch (RS) decreased. The maximum relative content of SDS of 34.41% was obtained under the following extrusion conditions: moisture content 25%, barrel temperature 70 ℃ and screw speed 140 r/min. When screw speed increased to 180 r/min with moisture content 40%, barrel temperature 70 ℃, the relative content of RS reached the minimum value of 10.49%. Particle size was positively correlated with SDS relative content and consistency coefficient (*K* value) (r = 0.60 and r = 0.61, P < 0.05). The extruded pea starch suspension was pseudoplastic. In frequency and temperature sweep tests, storage and loss moduli increased with the degree of starch damage increasing caused by extrusion. The results showed that the extruded pea starch exhibited enhanced structure and elastic gel properties. Therefore, extrusion can affect the *in vitro* starch digestibility and rheological properties of pea starch, thereby improving food functionality and quality.

Keywords: extrusion; pea starch; starch digestibility; rheological properties

挤压处理对豌豆淀粉的流变特性和体外消化率的影响

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摘　要：目的：研究挤压条件（豌豆淀粉水分质量分数：25%、35%、40%、45%和55%；剪切温度：50、60、70、80 ℃和90 ℃；螺杆转速：100、120、140、160 r/min和180 r/min）对豌豆淀粉的体外消化率和流变特性的影响。方法：采用体外消化法测定了豌豆淀粉的水解度，并通过稳态剪切实验、频率扫描实验和温度扫描实验测定了豌豆淀粉的流变特性。结果：挤压后水解度和慢消化淀粉（slowly digestible starch，SDS）相对含量增加，抗性淀粉（resistant starch，RS）相对含量降低；在水分质量分数为25%的条件下（螺杆转速140 r/min、剪切温度70 ℃），SDS相对含量最高，为34.41%；在螺杆转速为180 r/min时（水分质量分数40%、剪切温度70 ℃），RS相对含量最低，为10.49%。粒径与SDS相对含量和稠度系数*K*呈显著正相关（P＜0.05），相关系数分别为0.60和0.61。挤压的豌豆淀粉溶液为假塑性流体；在频率和温度扫描实验中，储存和损耗模量随豌豆淀粉挤压损坏程度增加而增加。结论：挤压后的豌豆淀粉结构增强并表现出弹性凝胶特性。因此，挤压工艺可能通过影响豌豆淀粉的体外消化率和流变性能来改善食品的功能性和品质。

关键词：挤压；豌豆淀粉；淀粉消化性；流变特性

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Peas, which are leguminous plants containing approximately 53% starch and 24% protein, are widely cultivated worldwide and contribute considerably to the total production of legumes[1]. The world's top four legume crops are soybean, peanuts, dry beans and peas[2]. Pea is a semi-hardy crop with short production cycle, low production cost and good market. In 2018, 1.49 million tonnes of dried peas have been consumed in China.

In daily diets, starch is the main source of carbohydrates and is an important source of energy for humans. Englyst et al[3] classified starch into three categories, namely, rapidly digestible (RDS), slowly digestible (SDS) and resistant (RS) starches. RDS and SDS are digested in the small intestine in 20 and 20–120 min, respectively, whereas RS is not digestible in the small intestine (> 120 min). However, it can be fermented by microorganisms in the large intestine to produce short-chain fatty acids. Extrusion, which has been used in the food and polymer industries since the 1940s, is a complex reaction process that can provide high pressure and temperature in a short time[4]. The use of a twin-screw extruders in food processing has steadily increased because its ability to change or mix with other materials to achieve the desired quality. Starch granules change from a compact structure to a loose polyhedral after extrusion, and from fewer pits to a numbers of cavities[5]. The relative crystallinity of extruded corn starch decreases and the crystal structure changes from the A-type pattern to V-type pattern, indicating that the structure becomes more thermally stable[6]. The SDS content decreases with increasing barrel temperature[7], and a moderate screw speed of 300 r/min and low moisture content results in high SDS and RS contents, respectively[8]. This technology has been widely used in the food and animal feed industries worldwide[9]. The extruded starch affects the characteristics and quality of a product. For instance, pea starch noodles prepared by using a twin-screw extruder has increased firmness, increased surface stickiness and reduced cooking loss[10]. Extruded wheat flour/pregelatinized cassava starch has reduced proofing and baking time and improves the quality of French bread made from frozen dough[11]. Extruded black gram flour improves the dough properties and enhances the sensory properties of the end product[12].

A number of studies have reported the characteristics of pea starch, such as high gel strength, high gelatinisation temperature, good transparency, easy retrogradation[1-2], *in vitro* digestibility and rheological characteristics[13-14]. However, these studies have not reported the effects of extrusion processes on the rheological and digestive properties of pea starch. Therefore, the aim of this work is to investigate the effect of extrusion on the *in vitro* digestibility, particle size and rheological properties of pea starch to improve the quality of pea starch-based products.

1 Materials and Methods

1.1 Materials and reagents

Native pea starch (NPS) Shandong Jianyuan Biological Engineering Co. Ltd.; Alpha-amylase from porcine pancreas (Cat. no. A3176, 19.6 U/mg) Sigma-Aldrich Co. Ltd. (Shanghai); Amyloglucosidase (EC3.2.1.3, 100 000 Units/mL) Shanghai Yuanye Bio-Technology Co. Ltd.; *D*-Glucose (GOPOD format) assay kit Ireland Megazyme Co. Ltd.; All other chemical reagents were analytical grade.

1.2 Instrument and equipment

UVTE36-24 Twin-screw extruder Hunan Chuangxiang Biotechnology Co. Ltd.; Matersize 2000 laser diffraction particle size analyzer, Kinexus lab + rotational rheometer UK Malvern Instrument Co. Ltd..

1.3 Methods

1.3.1 Measurement of pea starch chemical composition

The moisture, crude protein, starch, crude fat and ash contents of NPS was analysed in accordance with the methods described by Hu Lei et al[15]. Apparent amylose content was determined using the iodine reagent method[16].

1.3.2 Extrusion of pea starch

The extrusion process was carried out on a twin-screw extruder with the length to diameter ratio of 26. The parameters of the extrusion process were set as follows: feeding rate was constant at 15 kg/h; the temperatures in the first zone (feed zone), second zone (mix zone), fourth zone (screw conveying zone) and fifth zone (die) zones were 60, 90, 50 and 50 ℃, respectively, and the temperature in the third zone (shearing compression) was varied (50, 60, 70, 80 and 90 ℃), while maintained the screw speed at 140 r/min and the moisture content of samples was 40%; the moisture contents of pea starch were adjusted to 25%, 35%, 40%, 45% and 55% respectively by using an automatically controlled water influent device, while maintained the screw speed at 140 r/min and the temperature of the third zone at 70 ℃; the screw speed variations were 100, 120, 140, 160 and 180 r/min at a moisture content of 40% and the third zone temperature of 70 ℃. The extrudates were air-dried at room temperature, ground and passed through a 100-mesh sieve. All samples were dried to constant weight. The extrudates were denoted as 25M, 35M, 40M, 45M and 55M on the basis of the moisture content during extrusion; 50T, 60T, 70T, 80T and 90T on the basis of the extrusion temperature and 100R, 120R, 140R, 160R and 180R on the basis of the screw speed.

1.3.3 *In vitro* digestibility analysis

The RDS, SDS and RS contents and starch digestibility was measured using the Englyst's method[3] with some modifications. The enzyme solution was prepared by placing 1.3 g porcine pancreatin into a 50 mL centrifuge tube suspended in 20 mL distilled water. The mixture was stirred for 10 min by using a magnetic stirrer and centrifuged for 10 min at 5 000 r/min. The supernatant (17 mL) was collected and mixed with 2.55 μL amyloglucosidase.

Each sample (200 mg) was placed into a 50 mL tube, added with 20 mL sodium acetate buffer (0.1 mol/L, pH 5.2), sealed and mixed using a vortex mixer. The tube was placed into a water bath maintained at 100 ℃ for 30 min to completely gelatinise the starch. The tube was cooled to 37 ℃ and added with five glass balls (0.4 cm diameter) and 5 mL enzyme solution. The tube was sealed and placed into a shaking water bath (37 ℃, 200 times/min). Every 20 min, 0.1 mL of digestion solution was collected, then mixed with 1 mL 95% ethanol and centrifuged for 10 min at 5 000 r/min. The hydrolysed glucose content was measured using the *D*-glucose assay kit. Starch hydrolysis degree was calculated using the equation (1).

$$\text{Starch hydrolysis}/\% = \frac{0.9 \times \text{Gh}}{\text{Si}} \times 100 \quad (1)$$

Where Gh is the content of glucose produced/(mg/g); Si is the initial content of starch/(mg/g).

1.3.4 Measurement of particle size

Water was used as dispersing medium for all samples. Mechanical stirring (2 000 r/min) was applied to ensure uniform dispersion and particle distribution. The volume-weighted mean diameter *D*[4,3] was calculated using Mastersize 2000 laser diffraction particle size analyzer version 5.22 software.

1.3.5 Measurement of rheological properties

The rheological properties of extrudates were determined using the rotational rheometer equipped with a pair of coaxial cylinders. The inner and outer diameters were 25 and 27.5 mm, respectively. Rheological measurements were made at (25.00 ± 0.01) ℃. Solution of 10 g/100 mL was prepared for the tests.

1.3.5.1 Measurement of steady flow properties

The viscosity flow curves were obtained using a measuring cup and vanned rotor geometry with shear rate ranging from 0.1 to 100 s^{-1}. The Ostwald-de Waele model (equation (2)) was used to calculate the viscosity of all the samples.

$$\eta_{app} = K\gamma^{n-1} \quad (2)$$

Where η_{app} is the apparent viscosity/(Pa·s); γ is the shear rate/s^{-1}; K is the consistency coefficient/(Pa·s^n); n is the flow behaviour index (dimensionless) reflecting near-Newtonian flow. Linear regression analysis was applied to extrudates to calculate K and n.

1.3.5.2 Measurement of dynamic viscoelasticity

The dynamic viscoelastic properties were measured over a frequency range of 0.1–10 Hz, and a constant strain of 1% at 25 ℃ was used. The linear viscoelastic region was determined using strain sweeps at a frequency of 1 Hz at 25 ℃. The temperature sweep was recorded from 40–90 ℃ at a heating rate of 5 ℃/min, frequency of 1 Hz and controlled shear stress of 1 Pa. The storage (G'/Pa) and loss (G''/Pa) modulus responses were recorded. After heating, the samples were cooled immediately to 25 ℃. All tests were performed at least in triplicate.

1.4 Statistical analysis

Values were expressed as mean ± standard deviation of three replicates. Statistical differences were determined employing the Duncan's multiple range test ($P < 0.05$), and correlation analysis was performed employing the Pearson correlation coefficients by using the SPSS 17.0 software.

2 Results and Analysis

2.1 Chemical composition of NPS

NPS was composed of (15.46 ± 0.04)% moisture (wet basis), (83.75 ± 0.71)% starch (dry basis), (0.32 ± 0.04)% crude protein (dry basis), (3.41 ± 0.05)% crude fat (dry basis) and (0.06 ± 0.00) % ash (dry basis). The apparent amylose content was (34.56 ± 1.21)% (dry basis).

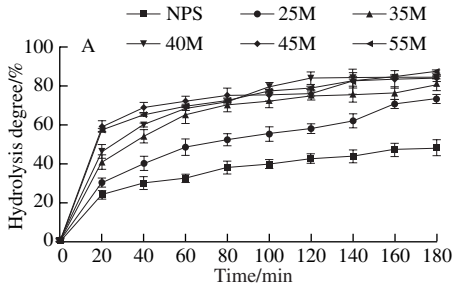
2.2 *In vitro* digestibility of NPS and the extrudates

The RDS, SDS and RS contents of the NPS and the extrudates were shown in Table 1. The enzymatic hydrolysis curves of the NPS and the extrudates are presented in Fig. 1. The starch hydrolysis rate of the NPS was much lower than that of the extrudates. The hydrolysis degree of NPS after 180 min was 48.42%. Results supported previous findings, which reported that legume starch, in its native form, was slowly digestible[17].

Table 1 Relative contents of RDS, SDS and RS and *D*[4,3] of native and extruded starch samples

Samples	RDS relative content/%	SDS relative content/%	RS relative content/%	*D*[4,3]/μm
NPS	20.42 ± 1.54^{k}	15.59 ± 1.58^{f}	47.73 ± 1.21^{a}	43.78 ± 0.23^{i}
25M	27.41 ± 1.57^{j}	34.41 ± 1.29^{a}	27.68 ± 1.02^{b}	366.66 ± 13.44^{a}
35M	35.66 ± 1.19^{gh}	32.07 ± 1.28^{bc}	12.10 ± 0.09^{gh}	260.27 ± 3.61^{bc}
40M	38.99 ± 1.08^{ef}	31.34 ± 1.04^{bc}	13.43 ± 0.98^{gh}	222.56 ± 0.68^{d}
45M	52.12 ± 0.47^{ab}	20.68 ± 1.43^{e}	13.69 ± 1.33^{fg}	204.90 ± 0.26^{f}
55M	53.66 ± 1.23^{a}	16.63 ± 1.39^{f}	16.03 ± 0.85^{e}	197.50 ± 1.14^{g}
50T	37.21 ± 1.12^{fg}	30.53 ± 1.33^{bc}	16.72 ± 1.56^{de}	190.18 ± 1.78^{h}
60T	37.96 ± 1.25^{f}	30.06 ± 1.41^{c}	15.76 ± 0.99^{ef}	197.24 ± 0.98^{g}
70T	38.99 ± 1.08^{ef}	31.34 ± 1.04^{bc}	13.43 ± 0.98^{gh}	222.56 ± 0.68^{d}
80T	41.20 ± 1.11^{d}	26.24 ± 1.48^{d}	12.13 ± 0.99^{gh}	210.24 ± 0.61^{ef}
90T	50.47 ± 1.10^{b}	20.91 ± 0.66^{e}	13.84 ± 1.55^{fg}	263.65 ± 1.94^{b}
100R	29.46 ± 1.05^{i}	30.94 ± 1.66^{bc}	21.11 ± 1.26^{c}	204.77 ± 0.49^{f}
120R	33.95 ± 1.17^{h}	31.89 ± 1.41^{bc}	18.49 ± 1.39^{d}	217.53 ± 0.43^{d}
140R	38.99 ± 1.08^{ef}	31.34 ± 1.04^{bc}	13.43 ± 0.98^{gh}	222.56 ± 0.68^{d}
160R	40.81 ± 1.38^{de}	33.92 ± 1.27^{ab}	11.47 ± 1.43^{hi}	211.65 ± 1.40^{e}
180R	43.42 ± 1.08^{c}	28.11 ± 1.50^{cd}	10.49 ± 1.28^{i}	255.70 ± 0.38^{c}

Note: Values within the same column with a different superscript letter are significantly different ($P < 0.05$). The same as Table 3.



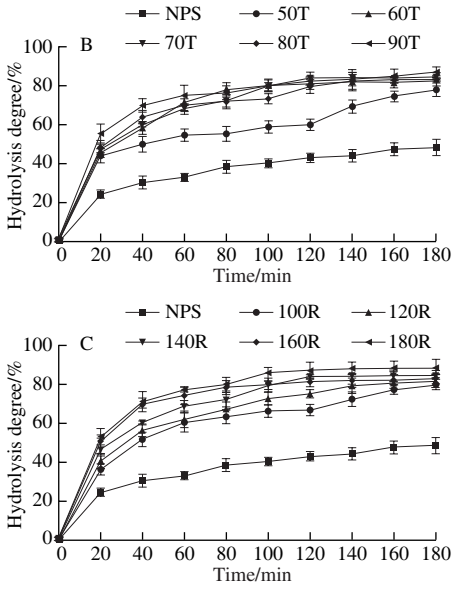


Fig. 1 Influence of moisture content (A), barrel temperature (B) and screw speed (C) on digestibility of extruded pea starch

The hydrolysis degrees for extrudates were higher than those of 25M and 35M extrudates (Fig. 1A). Furthermore, the hydrolysis degree after 180 min was highest for the 55M extrudate, indicating the higher digestibility of extrudates at higher moisture content. The 25M extrudate had the lowest RDS and the highest SDS contents (Table 1). Moisture increases the heat capacity, which reduces the physicochemical transformation in the extrudates[18]. Low moisture content created a severe condition in the extruder due to lack of water lubrication, resulting in the increase of the starch fragmentation. Therefore, short starch polymers were generated after cooling for increased molecular mobility, thereby increasing the SDS content[8].

With all the variables kept constant (moisture content of 40% and screw speed of 140 r/min), NPS was extruded at 50–90 ℃. The relationship between the barrel temperature and the starch hydrolysis degree of pea starch is shown in Fig. 1B. At 180 min, the hydrolysis degree increased from 78.03% to 87.26% as the barrel temperature increased from 50 ℃ to 90 ℃. During extrusion at limited moisture content (40%), more heat is required for starch gelatinisation[19], which means that higher temperature results in higher gelation of starch, making it more susceptibility to enzymatic digestion. Furthermore, the hydrogen bonds between the starches have been disrupted, and extreme starch chain mobility contributes to high hydrolysis degree[12]. Some reports have evaluated the effect of extrusion temperature on starch digestibility and revealed similar results[10,20].

Starch was extruded at screw speeds of 100–180 r/min at 40% moisture content and 70 ℃. The behaviour of

the hydrolysis of extrudates with respect to screw speeds is shown in Fig. 1C. The hydrolysis degree increased with the increase of screw speed. This observation was explained on the basis of the high shear force in the extruder led to increasing the degree of molecular degradation.

The relative contents of RDS, SDS and RS of NPS and extrudates were shown in Table 1. NPS showed higher RS relative content (47.73%) than extrudates (10.49%–27.68%), which suggested that the chain activity was limited in NPS, and the breakdown of starch during extrusion changed the structure organisation of the starch molecules, thereby changing their susceptibility to enzymatic hydrolysis[21]. Increased sensitivity to enzymatic hydrolysis following extrusion has been observed in whole grain oats and lentil split[8,22]. SDS is generally the most desirable form of dietary starch[17]. The optimum moisture content, barrel temperature and screw speed for the highest SDS content were 25%, 70 ℃ and 160 r/min, respectively.

In summary, extrusion treatment increased *in vitro* starch digestibility, RDS relative content, and decreased the RS relative content. The Pearson correlation coefficients of the digested properties of extrudates are shown in Table 2. SDS relative content was negatively associated with RDS relative content ($r = -0.63$, $P < 0.01$).

Table 2 Pearson correlation coefficients among *in vitro* digestibility, particle size and consistency coefficient of extrudates

Indicators	Hydrolysis degree	RDS relative content	SDS relative content	RS relative content	D[4,3]	K
Hydrolysis degree	1					
RDS relative content	0.81**	1				
SDS relative content	−0.39	−0.63**	1			
RS relative content	−0.75**	−0.60*	0.55*	1		
D[4,3]	−0.40	−0.47	0.60*	0.49	1	
K	0.19	0.23	0.24	0.05	0.61*	1

Note: *. Significant correlation ($P < 0.05$); **. Extremely significant correlation ($P < 0.01$).

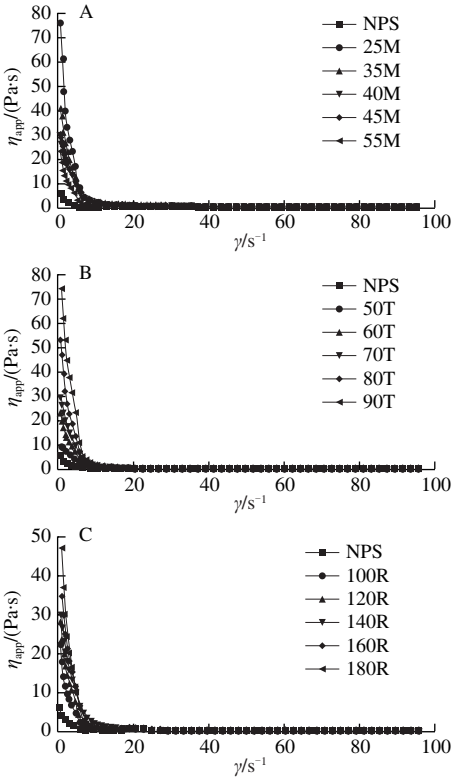
2.3 Particle size of NPS and the extrudates

The particle sizes of all samples are shown in Table 1. The Pearson correlation (Table 2) demonstrated moderately relevant relationship between D[4,3] and hydrolysis degree ($r = -0.40$, $P > 0.05$), RDS relative content($r = -0.47$, $P > 0.05$) and RS relative content ($r = 0.49$, $P > 0.05$). These findings suggested that the D[4,3] was not the main factor influencing the digestibility properties under the conditions of the present study. However, D[4,3] had positive association and with the SDS relative content ($r = 0.60$, $P < 0.05$) and K ($r = 0.61$, $P < 0.05$) of the extrudates. This result agreed with the results of Svihus et al[23], which showed the relationship between water affinity and specific surface area.

2.4 Rheological properties of NPS and the extrudates

2.4.1 Steady shear test

The flow curves of the samples are presented in Fig. 2. The η_{app} can be described using the Ostwald-de Waele model ($R^2 > 0.93$) in the range of γ from 0.1 to 100 s^{-1}, which showed the strong dependence of η_{app} on γ. This result indicates a significant increase in η_{app} for the extrudates, which can be primarily attributed to the arrangement of the particles in the samples and breakdown of their interactions under the influence of the γ[24].



A–C. represents the influence of moisture content, temperature, screw speed, respectively.

Fig. 2 Rheological curves of native and extruded pea starch suspensions

The K and n values of the different samples are shown in Table 3. K decreased as the moisture content increased but increased as the barrel temperature and screw speed increased. In addition, all n values were less than 1, which indicated that the flow curves presented the shear thinning or pseudoplastic behaviour (η_{app} decreased with the increased of γ).

The pea starch was partially gelatinised after extrusion, which led to high viscosity. The difference amongst the consistency coefficients for all extrudates may be attributed to the differences in particle size[25]. Positive relationships were observed between particle size and K ($r = 0.61$, $P < 0.05$) (Table 2). These results suggested that the disruption and resistance of swollen large starch granules were responsible

for the shear thinning behaviour at low γ. At high γ, amylose entangles shrinks, lixiviates from the swollen granules and forms the stabilised network structure.

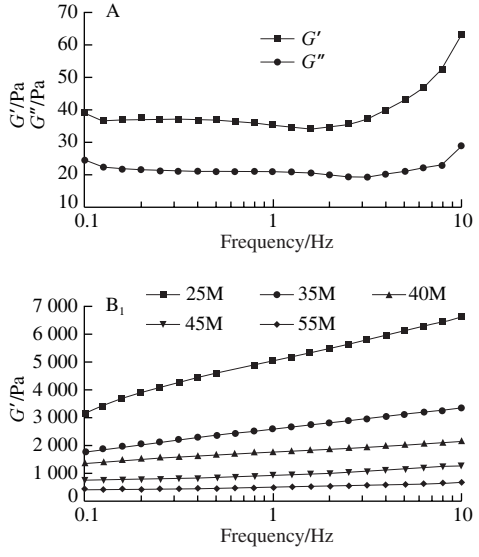
Table 3 Parameters of the Ostwald-de Waele model describing the shear thinning behaviour of samples

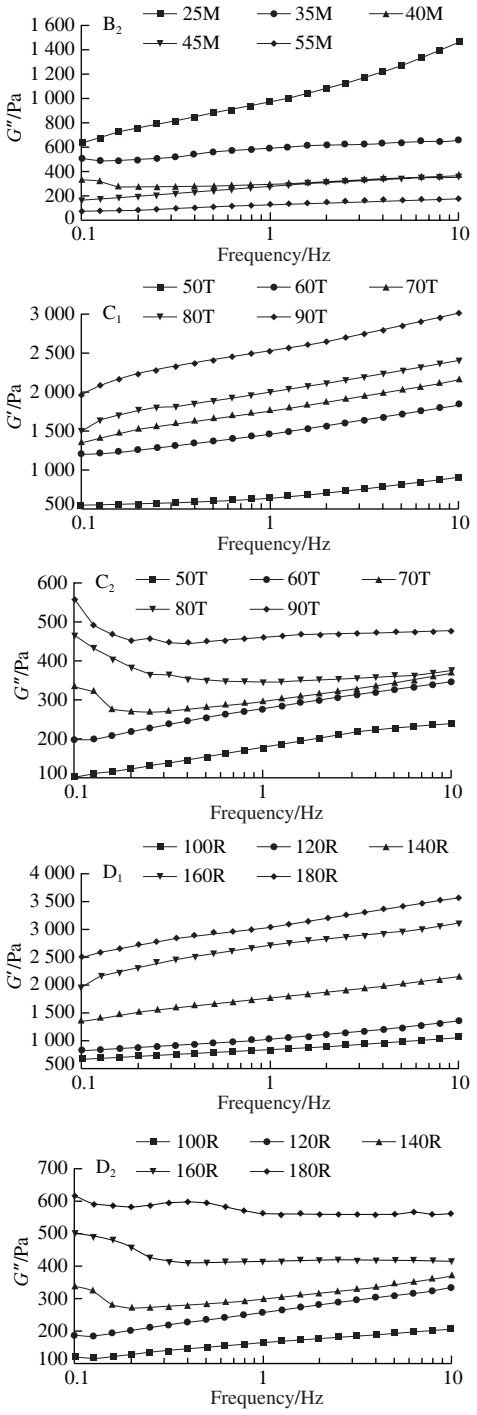
Samples	K/(Pa·s^n)	n	R^2
NPS	8.20^{i}	−0.42^{fg}	0.93
25M	69.04^{b}	−0.36^{i}	0.97
35M	46.39^{e}	−0.27^{k}	0.98
40M	41.32^{f}	−0.31^{j}	0.99
45M	40.90^{f}	−0.43^{f}	0.96
55M	37.77^{g}	−0.53^{b}	0.99
50T	25.69^{h}	−0.43^{f}	0.97
60T	41.52^{f}	−0.45^{e}	0.99
70T	41.32^{f}	−0.31	0.99
80T	61.52^{c}	−0.39^{h}	0.98
90T	97.20^{a}	−0.57^{a}	0.96
100R	25.33^{h}	−0.49^{cd}	0.99
120R	38.28^{g}	−0.48^{d}	0.99
140R	41.32^{f}	−0.31	0.99
160R	47.68^{e}	−0.50^{c}	0.97
180R	53.38^{d}	−0.41^{g}	0.97

2.4.2 Dynamic viscoelasticity tests

2.4.2.1 Frequency sweep test

The mechanical spectra obtained at 25 ℃ for G' and G'' of the different rheological parameters from the NPS and the extrudates are presented in Fig. 3. The plateau relaxation zone was observed in all samples at low frequencies. The area of G' was higher than that of G'', and both moduli depend on frequency but follow different patterns[24]. Fig. 3 showed strong frequency dependence, which indicated that the material structure had molecular entanglement[26].





A. SNP; B–D. represents the influence of moisture content, temperature, screw speed, respectively; Subscript 1. G'; Subscript 2. G''. The same as Fig. 4.

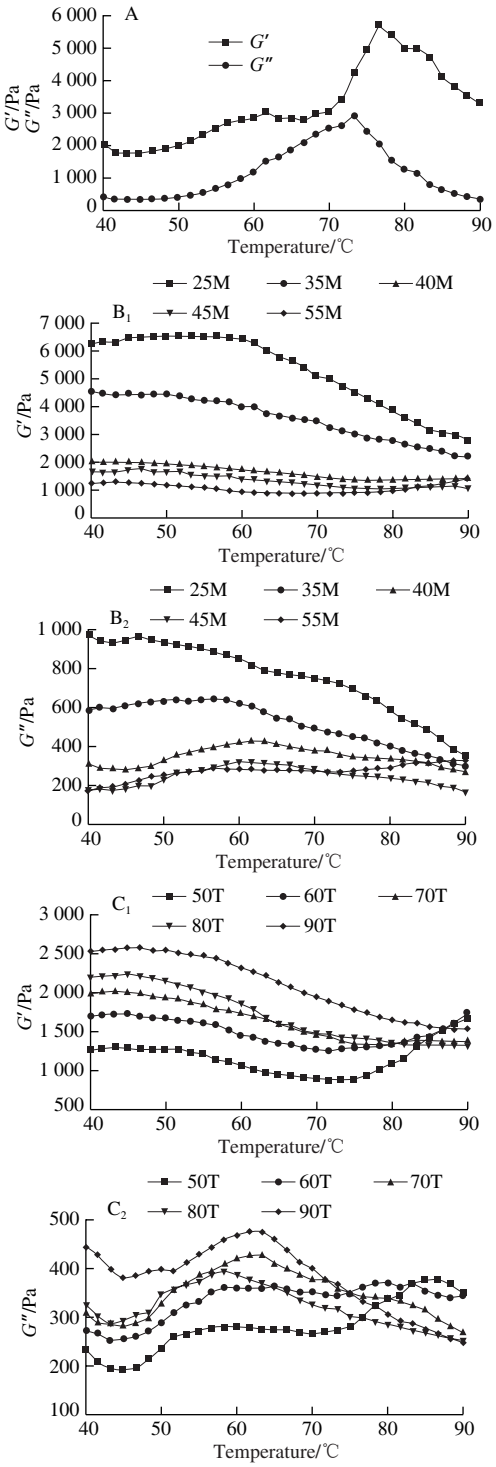
Fig. 3 Elastic (G') and loss (G'') moduli dependence on frequency as obtained from frequency sweep test at 1% strain

The dynamic moduli increased with the severity of the pea starch extrusion process, i.e., with increasing extrusion temperature and barrel speed and with decreasing moisture content. The G' of the NPS and the extrudates increased with an increase in frequency from 0.1 to 10 Hz. G' was higher than G'', indicating that the elastic behaviour was

superior than the viscous behaviour. Wani et al[27] has reported comparable results on the flow behaviour for Bengal gram starch, which may be due to the extension and intertwining of molecular chains in the extrudates, leading to their structural reorganisation due to the continuous increase in frequency. However, G'' showed various trends under different extrusion conditions. At relatively high barrel temperatures (70, 80 and 90 ℃) and screw speeds (140, 160 and 180 r/min), the G'' slightly decreased with increasing frequency and stabilized gradually. In addition to these conditions, G'' increased with increasing frequency. The probability of such behaviour may be linked to the gelatinised starch molecules that were dispersed under the external force to reduce its G'' at the beginning and aggregated and stabilised. The starch granules were partially destroyed due to the relatively low screw speed and barrel temperature. Therefore, the increase in G'' caused by molecular rupture was offset by the decreased external force. According to the flow curves, these results demonstrated that the extruded starch can enhance the structure and increase G' and G'' because of extrudates' high-water absorption capacity.

2.4.2.2 Temperature sweep test

G' and G'' curves versus temperature for NPS and extrudates at selected temperature (40–90 ℃) were reported in Fig. 4. For the NPS, the G' and G'' initially increased to a maximum value and then decrease with temperature increasing. Viscoelastic properties were greatly influenced by swollen starch granules in the heated starch system[28], and the heating process promotes the close association of the gelatinized and swollen starch granules, increasing the mobility and collision of these swollen granules[29]. The decrease in G' may be attributed to the breakdown of starch granules and destruction of the intermolecular interactions, which finally resulted in decreased degree of chain entanglements[29]. Ji Zhili et al[30] studied the rheological properties of corn starch and reported similar results. Compared with NPS, the G' of the extrudates decreased from 60 ℃. The degree of decline was proportional to the severity of the starch. This observation indicated that extrusion ruptured the starch granules, resulting in the quick water absorption of partially gelatinised starch, which led to the lower G' of the extrudates than that of the NPS except 25% and 35% moisture content. At higher extrusion temperature conditions, less damaged starch granules were less susceptible to water loss, causing an increase in G'. However, the G'' curves were observed to initially increase and decline, which was also observed in extrudes with high screw speeds (140, 160 and 180 r/min) or with high barrel temperature (70, 80 and 90 ℃), which indicated that the pea starch had better viscosity capacity under relative extreme extrusion conditions. It had been considered that starch suspensions with $G' > 500$ Pa and tan θ (G''/G') < 0.2 during temperature sweep could be regarded as an elastic gel[31], which indicates that the pea starch suspensions converted to an elastic gel after extrusion process.



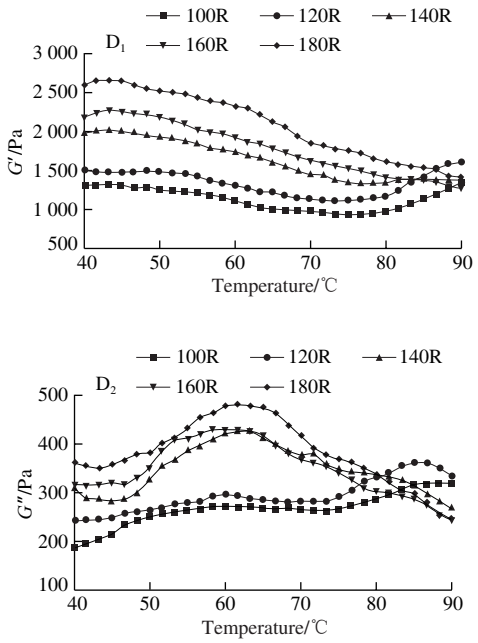


Fig. 4 Elastic (*G*′) and loss (*G*″) moduli of native and extruded pea starch

3 Conclusion

The *in vitro* digestibility, rheological properties and particle size of the NPS and the extrudates were determined. The hydrolysis degree of the extrudates differed in different moisture contents, barrel temperatures and screw speeds. Pea starch was gelatinised and disrupted in the extruder, increasing the accessibility of the digestive enzymes to the starch granules. The minimum RS relative content was obtained at 180 r/min (180R), whereas the maximum SDS relative content was obtained at 25% moisture content (25M). Based on the Ostwald-de Waele model, the rheological analysis showed that the NPS and the extrudates were affected by particle size. For frequency sweep from 0.1 to 10 Hz, the G' and G'' were dramatically increased in the extrudates compared with that of NPS because the former obtained higher water absorption capacity and enhanced structure than the latter. G' was higher than G'', indicating that the elastic behaviour was better than the viscous behaviour for extrudates. For the temperature sweep, G' and G'' were negatively associated with moisture content and positively associated with barrel temperature and screw speed. Although further investigations are required to fully understand the mechanisms of the changes in pea starch in the extruder, the trends obtained are important for the development of new pea starch-based foods and the optimisation of extrusion processes.

References:

[1] ZHANG Y P, ZHUANG K, DING W P, et al. Comparison of physicochemical properties of pea starch, potato starch and corn starch[J]. Science and Technology of Food Industry, 2016, 37(4): 183-186. DOI:10.13386/j.issn1002-0306.2016.04.028.

[2] RATNAYAKE W S, HOOVER R, WARKENTIN T. Pea starch: composition, structure and properties: a review[J]. Starch-Stärke, 2002, 54(6): 217-234. DOI:10.1002/1521-379X(200206)54:6<217::AID-STAR217>3.0.CO;2-R.

[3] ENGLYST H N, KINGMAN S M, CUMMINGS J H. Classification and measurement of nutritionally important starch fractions[J]. European Journal of Clinical Nutrition, 1992, 46(2): 33-50. DOI:10.1128/IAI.01649-06.

[4] JOZINOVIĆ A, ŠUBARIĆ D, AČKAR Đ, et al. Influence of spelt flour addition on properties of extruded products based on corn grits[J]. Journal of Food Engineering, 2016, 172: 31-37. DOI:10.1016/j.jfoodeng.2015.04.012.

[5] ROMÁN L, GÓMEZ M, HAMAKER B R, et al. Banana starch and molecular shear fragmentation dramatically increase structurally driven slowly digestible starch in fully gelatinized bread crumb[J]. Food Chemistry, 2019, 274: 664-671. DOI:10.1016/j.foodchem.2018.09.023.

[6] YAN X, WU Z Z, LI M Y, et al. The combined effects of extrusion and heat-moisture treatment on the physicochemical properties and digestibility of corn starch[J]. International Journal of Biological Macromolecules, 2019, 134: 1108-1112. DOI:10.1016/j.ijbiomac.2019.05.112.

[7] LICATA R, CHU J Y, WANG S L, et al. Determination of formulation and processing factors affecting slowly digestible starch, protein digestibility and antioxidant capacity of extruded sorghum-maize composite flour[J]. International Journal of Food Science & Technology, 2014, 49(5): 1408-1419. DOI:10.1111/ijfs.12444.

[8] BRAHMA S, WEIER S A, ROSE D J. Effects of selected extrusion parameters on physicochemical properties and *in vitro* starch digestibility and β-glucan extractability of whole grain oats[J]. Journal of Cereal Science, 2016, 70: 85-90. DOI:10.1016/j.jcs.2016.05.001.

[9] ATHAR N, HARDACRE A, TAYLOR G, et al. Vitamin retention in extruded food products[J]. Journal of Food Composition and Analysis, 2006, 19(4): 379-383. DOI:10.1016/j.jfca.2005.03.004.

[10] WANG N, MAXIMIUK L, TOEWS R. Pea starch noodles: Effect of processing variables on characteristics and optimisation of twin-screw extrusion process[J]. Food Chemistry, 2012, 133(3): 742-753. DOI:10.1016/j.foodchem.2012.01.087.

[11] ORTOLAN F, BRITES L T G, MONTENEGRO F M, et al. Effect of extruded wheat flour and pre-gelatinized cassava starch on process and quality parameters of French-type bread elaborated from frozen dough[J]. Food Research International, 2015, 76: 402-409. DOI:10.1016/j.foodres.2015.07.010.

[12] ANANTHANARAYAN L, GAT Y, PANGHAL A, et al. Effect of extrusion on thermal, textural and rheological properties of legume based snack[J]. Journal of Food Science and Technology, 2018, 55(9): 3749-3756. DOI:10.1007/s13197-018-3306-8.

[13] UTRILLA-COELLO R G, RODRÍGUEZ-HUEZO M E, CARRILLO-NAVAS H, et al. *In vitro* digestibility, physicochemical, thermal and rheological properties of banana starches[J]. Carbohydrate Polymers, 2014, 101: 154-162. DOI:10.1016/j.carbpol.2013.09.019.

[14] JUNG D S, BAE I Y, HAN S I, et al. Classification of hydrocolloids based on *in vitro* starch digestibility and rheological properties of Segoami gel[J]. International Journal of Biological Macromolecules, 2017, 104: 442-448. DOI:10.1016/j.ijbiomac.2017.06.063.

[15] HU Lei, GUO Jiamin, ZHU Xiwei, et al. Effect of steam explosion on nutritional composition and antioxidative activities of okra seed and its application in gluten-free cookies[J]. Food Science & Nutrition, 2020, 8: 4409-4421. DOI:10.1002/fsn3.1739.

[16] KONG X L, ZHU P, SUI Z Q, et al. Physicochemical properties of starches from diverse rice cultivars varying in apparent amylose content and gelatinisation temperature combinations[J]. Food Chemistry, 2015, 172: 433-440. DOI:10.1016/j.foodchem.2014.09.085.

[17] SANDHU K S, LIM S T. Digestibility of legume starches as influenced by their physical and structural properties[J]. Carbohydrate Polymers, 2008, 71(2): 245-252. DOI:10.1016/j.carbpol.2007.05.036.

[18] MAHASUKHONTHACHAT K, SOPADE P A, GIDLEY M J. Kinetics of starch digestion and functional properties of twin-screw extruded sorghum[J]. Journal of Cereal Science, 2010, 51(3): 392-401. DOI:10.1016/j.jcs.2010.02.008.

[19] SUN Z H, YANG W D, SIEBENMORGEN T S, et al. Thermomechanical transitions of rice kernels[J]. Cereal Chemistry, 2002, 79(3): 349-353. DOI:10.1094/CCHEM.2002.79.3.349.

[20] LICATA R, COOREY R, ZHAO Y, et al. Maximizing slowly digested starch in an expanded sorghum-maize extruded food using response surface methodology[J]. Starch-Stärke, 2015, 67(3/4): 285-293. DOI:10.1002/star.201400191.

[21] YE J P, LIU C M, LUO S J, et al. Modification of the digestibility of extruded rice starch by enzyme treatment (*β*-amylolysis): an *in vitro* study[J]. Food Research International, 2018, 111: 590-596. DOI:10.1016/j.foodres.2018.06.002.

[22] RATHOD R P, ANNAPURE U S. Effect of extrusion process on antinutritional factors and protein and starch digestibility of lentil splits[J]. LWT-Food Science and Technology, 2016, 66: 114-123. DOI:10.1016/j.lwt.2015.10.028.

[23] SVIHUS B, UHLEN A K, HARSTAD O M. Effect of starch granule structure, associated components and processing on nutritive value of cereal starch: a review[J]. Animal Feed Science and Technology, 2005, 122(3/4): 303-320. DOI:10.1016/j.anifeedsci.2005.02.025.

[24] MARTÍNEZ M M, SANZ T, GÓMEZ M. Influence of wheat flour subjected to different extrusion conditions on the rheological behaviour and thermal properties of batter systems for coating[J]. LWT-Food Science and Technology, 2015, 64(2): 1309-1314. DOI:10.1016/j.lwt.2015.07.037.

[25] SINGH N, SINGH J, SODHI N S. Morphological, thermal, rheological and noodle-making properties of potato and corn starch[J]. Journal of the Science of Food and Agriculture, 2002, 82(12): 1376-1383. DOI:10.1002/jsfa.1194.

[26] SINGH J, KAUR L, MCCARTHY O J. Factors influencing the physico-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications: a review[J]. Food Hydrocolloids, 2007, 21(1): 1-22. DOI:10.1016/j.foodhyd.2006.02.006.

[27] WANI I A, FAROOQ G, QADIR N, et al. Physico-chemical and rheological properties of Bengal gram (*Cicer arietinum* L.) starch as affected by high temperature short time extrusion[J]. International Journal of Biological Macromolecules, 2019, 131: 850-857. DOI:10.1016/j.ijbiomac.2019.03.135.

[28] LII C Y, TSAI M L, TSENG K H. Effect of amylose content on the rheological property of rice starch[J]. Cereal Chemistry, 1996, 73(4): 415-420. DOI:10.1021/bp960041s.

[29] CHEN H, XIE F W, CHEN L, et al. Effect of rheological properties of potato, rice and corn starches on their hot-extrusion 3D printing behaviors[J]. Journal of Food Engineering, 2019, 244: 150-158. DOI:10.1016/j.jfoodeng.2018.09.011.

[30] JI Zhili, YU Long, LIU Hongsheng, et al. Effect of pressure with shear stress on gelatinization of starches with different amylose/amylopectin ratios[J]. Food Hydrocolloids, 2017, 72: 331-337. DOI:10.1016/j.foodhyd.2017.06.015.

[31] LII C Y, SHAO Y Y, TSENG K H. Gelation mechanism and rheological properties of rice starch[J]. Cereal Chemistry, 1995, 72(4): 393-400.