doi: 10.17221/125/2015-CJFS

Effect of Extrusion Treatment with Different Emulsifiers on the Thermal Stability and Structure of Corn Starch

Qingyu YANG[1,2], Zhigang XIAO[1], Yan ZHAO[1], Chunjing LIU[1], Yan XU[1] and Junkun BAI[1]

[1]College of Food Science, Northeast Agricultural University, Harbin, P.R. China;
[2]Food and Bioengineering College, Oiqihar University, Qiqihar, P.R. China

Abstract

Yang Q.-Y., Xiao Z.-G., Zhao Y., Liu Ch.-J., Xu Y., Bai J.-K. (2015): **Effect of extrusion treatment with different emulsifiers on the thermal stability and structure of corn starch**. Czech J. Food Sci., 33: 464–473.

Corn starch was treated with raw moisture (30%), screw speed (160 rpm), extrusion temperature (30, 55, 80, 105, 130, and 155°C), and emulsifier (1.2%) to produce the starch extrudate particles in a twin screw extruder. The influence of extrusion processing and composition (starch and emulsifier content) on the viscosity, microstructure, solubility, swelling power, and thermal stability of starch extrudate particles was examined. The SEM results showed that the surface of starch extrudate particles was quite irregular and a fissure could be clearly observed. The X-ray intensities and relative crystallinity were decreased after extrusion treatment. The data highlighted that the gelatinisation temperature and solubility were increased and the gelatinisation enthalpy, viscosity, and swelling power were decreased. The emulsifiers present also influenced the thermal stability and solubility of starch extrudate particles, which were attributed to their ability to modify starch granule interactions. The thermogravimetric analysis and differential scanning calorimetry analysis indicated that the thermal stability of starch extrudate particles was improved after extrusion processing.

Keywords: crystallinity; modified starches; extrudate; complexes

In recent years, there has been a consideration focused on the modification of starch by extrusion processing in the food industry area (Moad 2011). Starch is a bio-renewable natural polymer and can be transformed into thermoplastic starch (TPS) through thermomechanical treatment (Zhang *et al.* 2013). Starch and its derivations are widely applied in many areas such as food, medicine, textile paper, and oil exploration fields (Lazou & Krokida 2010; Yu *et al.* 2012). The modification of starch particles which act as thickeners and gelling agents in the food area has been known for many years. However, different applications have different requirements regarding starch specific properties. Some inherent structure limitations of natural corn starch utilisation (for example, insoluble in cold water, unstable paste under acid, heat and shear force) restrict its wider applications. In order to improve its properties to meet the requirements for specific characteristics and to raise its nutritional value, more attention is being paid to develop and process the modified starches. Generally speaking, starch modification mainly includes chemical, enzymatic, and physical modification methods. Compared with the physical method, the chemical modification may produce pollutant discharge and the enzymatic modification is relatively complex and not easy to control. Therefore, the physical method has been receiving increasingly more and more attention recently. Extrusion treatment is commonly used for processing thermoplastic starch, providing a stable, continuous process (Li *et al.* 2014). The extrusion processing is a form of starch modification that occurs at a high temperature and within a short time and is an important physical method that is simple, environmentally safe, and low cost. Extrusion processing, as a novel physical method in starch modification, will be applied on a larger scale in the food area. Extrusion processing of starch-based materials involves multiple chemical and physical reactions, e.g. water diffusion, granule expansion, gelatinisation, decomposition, melting, and crystallisation (Choi & Kerr 2003; Singh *et al.* 2007). Due to the multiphase transitions of starch, the microstructure and mechanical properties of starch-

doi: 10.17221/125/2015-CJFS

based materials strongly depend on the extrusion conditions (Liu *et al.* 2014; Martinez *et al.* 2014).

Sucrose esters (SE) have been commercially manufactured as food emulsifiers since the early 1960s (Szűts & Szabó-Révész 2012). Glycerol monostearate (GMS) is a colourless, odourless, and sweet-tasting flaky powder that is hygroscopic, so it is widely used as an emulsifier in the food industry (Galloway *et al.* 1989; Carrillo-Navas *et al.* 2014). Calcium stearoyl lactylate (CSL) is used to enhance dough conditioners/strengtheners and softeners in starch products (Gomes-Ruffi *et al.* 2012). The diacetyl tartaric acid ester of monoglycerides (DATEM) has been shown to modify the resistance and extensibility of dough by different proposed mechanisms (Ponzio *et al.* 2013). The SE, CSL, DATEM, and GMS have also been noted as good emulsifying and stabilising agents in the food processing field (De Pilli *et al.* 2007; Szűts & Szabó-Révész 2012). Thus, an emulsifier is usually added to cereal food to produce the desired specific characteristics (De Pilli *et al.* 2007). As the amylose in starch tends to form inclusion polymers with hydrophobic ligands, such as lipids, fatty acids, and esters (Singh *et al.* 1998; Ali & Hasnain 2013), the emulsifiers are often used in the food processing area to improve food properties (Krog 1973). There are cationic, anionic and nonionic emulsifiers, but cationic emulsifiers are rarely used as food emulsifiers. DATEM and CSL are anionic, but SE and GMS are nonionic. Thus, anionic and nonionic emulsifiers were investigated in this study. De Pilli *et al.* (2007) studied the oil loss and structural characteristics of wheat flour starch extrudate particles after extrusion process. Azizi and Rao (2005) studied the pasting properties of corn starch with addition of different surfactants (glycerol monostearate, distilled glycerol monostearate, sodium stearoyl-2-alactylate, and diacetyl tartaric acid esters of monoglyceride) in a water system at different temperatures. Conde-Petit and Escher (1995) discussed the rheology of starch emulsifier complexes at different moisture levels. However, the thermal stability of corn starch extrudate particles has been studied very little, and also little detailed studies on the relationship between the structure and thermal stability of corn starch extrudate particles are available. Thus, the thermodynamic properties of corn starch extrudate particles need to be further studied.

The objective of the present study was to precisely examine the role of emulsifiers and extrusion processing conditions on the thermal stability and structural characteristics of starch extrudate particles. The mixture of starch and emulsifier were extruded and then their structure and thermal stability were characterised. Our focus was to understand the different contributions that starch and emulsifiers made to the overall physico-chemical properties of the mixed systems. This experiment provided a method to improve the thermal stability and solubility of starch in the food processing area.

MATERIAL AND METHODS

Raw materials. Native corn starch (NS) (25% amylose) was supplied by Changchun Dacheng Group Co., Ltd. (Changchun, China), calcium stearoyl lactylate (CSL) and diacetyl tartaric acid esters of monoglyceride (DATEM) from Henan Yuzhong Biological Tech Co., Ltd. (He'nan, China), sucrose fatty acid ester (SE) from Adana Food Tech Co., Ltd. (Guangxi, China), and glycerol monostearate (GMS) from Zhang Jia Gang Zhong Ding Additive Co., Ltd. (Jiangsu, China). All other chemicals and solvents were of analytical grade.

Extrusion conditions. Extrusion was carried out in a co-rotating twin screw extruder (EV25; Clextral, Firminy, France). The barrel length (L) was 400 mm and the screw diameter (D) was 25 mm (L/D = 16). The diameter of extruder die was 4.0 mm. In this study, all extrusion parameters (e.g. screw speed of 160 rpm and raw moisture of 30%) were kept constant. The screw barrel was segmented into six temperature controlled zones. The barrel temperatures from segment 1 to 6 were 30, 55, 80, 105, 130, and 155°C, respectively. The extruder was operated at a constant feed rate of 10 kg/hours. When the barrel temperature exceeded 170°C, the extruder could not be successfully operated and the colour of starch extrudates became darker, which was not suitable for application in the food processing industry. The preliminary experiments showed that the parameters mentioned above were the optimal extrusion processing conditions. Approximately 1000 g of the dried corn starch were mixed with four different emulsifiers: 1.2 CSL, 1.2 GMS, 1.2 DATEM, and 1.2% SE. When the emulsifier addition exceeded 1.2%, the thermal stability and solubility exhibited no significant difference. We adjusted the moisture of corn starch and emulsifier mixture by 30%. The emulsifiers were dissolved in hot water at 55°C and then the emulsifier solution and corn starch were

doi: 10.17221/125/2015-CJFS

blended together. The corn starch and the emulsifier were mixed in a solid mixer (Prodima MJ50; Prodema Engineering AG, Bronschhofen, Switzerland) and then introduced into the extruder using a co-rotating twin screw feeder (K-Tron Co, Niederlenz, Switzerland). The starch extrudate particles were collected by filtration, washed with 70% aqueous solution of ethanol and centrifuged at 3200 *g* for 15 minutes. This process was repeated twice to eliminate impurities. After filtration, residual ethanol was removed by evaporation in the air, and the starch extrudate particles were dried at 50°C overnight and weighed. The starch extrudate particles were finally ground and passed through a 150 μm sieve and then stored in a desiccator for further analysis. The extrusion processing experiments were performed in triplicate.

Scanning electron microscopy (SEM). The surface structure of the native corn starch and corn starch extrudate particles was observed by scanning electron microscopy. Starch samples were mounted on circular aluminium stubs with double sticky tape, coated with 20 nm of gold and examined and photographed in a scanning electron microscope (S-3400N; Hitachi, Tokyo, Japan) at an accelerating potential of 20 kV.

Swelling power and solubility. Swelling power (SP) and solubility (S) of starch were determined in the temperature range from 55°C to 95°C, using the method of Wang *et al.* (2014) with a slight modification. 500 mg (dry basisi – db) of samples were accurately weighed and quantitatively transferred into a clear dried test tube and weight. Then 20 ml distilled water was added to the test tube and the mixture was mixed thoroughly for 30 seconds. The resultant slurries were heated at desired temperatures of 55, 65, 75, 85, and 95°C for 30 min in a water bath. The mixture was cooled to room temperature and then centrifuged (5000 *g*, 15 min). The supernatant was decanted carefully and kept, and the residue was weighed for SP determination (W_t). The supernatant was poured into a glass dish and then dried to a constant weight at 110°C (W_r). The swelling power and solubility measurements were performed in triplicate. The solubility and swelling power were estimated as follows:

$$\text{Solubility (\%)} = (W_r/W) \times 100 \qquad (1)$$

$$\text{Swelling power (\%)} = \frac{W_t \times 100}{W\,(100 - \mathrm{S})} = \frac{W_t}{\mathrm{W}\,(1 - \mathrm{S}/100)} \qquad (2)$$

where: W – dry weight of starch samples; W_r – weight of the dried supernatant; W_t – weight of the sediment starch (mg); S – solubility

Pasting properties. Pasting properties of native corn starches and corn starch extrudate particles were measured using a Rapid Visco Analyzer RAV (RAV-4; Newport Scientific, Warriewood, Australia). Three gram sample of solids (db) and 20 ml of distilled water were placed in an aluminium canister. A starch slurry was subjected to a controlled heating and cooling cycle under constant shear rate where it was heated from 50°C to 95°C at 12°C/min (after an equilibration time of 1 min at 50°C), held at 95°C for 2.5 min, cooled to 50°C at 12°C /min, and held at 50°C for 2 minutes. The pasting temperature (PT), peak viscosity (PV), trough viscosity (TV), breakdown (BD), final viscosity (FV), and setback (SB) were obtained. All results presented are the average of triplicate parallel experiments.

X-ray powder diffractometry. X-ray powder diffraction patterns were obtained with an X-ray powder diffractometer (D8-Advance; Bruker, Karlsruhe, Germany) following the method of Sun *et al.* (2014) with a slight modification. The scanning region of the diffraction angle (θ) was 3–35° at a step size of 0.6 seconds. Traces were obtained using a Cu-Kα radiation detector with a nickel filter and scintillation counter operating under the following conditions: 40 kV, 200 mA, 1°/1° divergence slit/scattering slit, 0.30 mm receiving slit, 1 s time constant, and scanning rate of 2°/min at room temperature. The relative crystallinity (X_c) was calculated in accordance with the method of Miao *et al.* (2009) as follows:

$$X_c\,(\%) = \frac{A_c}{A_c + A_n} \times 100 \qquad (3)$$

where: A_c, A_n – areas of crystalline or amorphous regions

All tests were performed in triplicate and the average values were reported

Differential scanning calorimetry (DSC). The thermal characteristics of corn starch and corn starch extrudate particles were measured using a differential scanning calorimeter (DSC-Q20; TA Instruments, New Castle, USA). A total weight of 3.0 mg of starch samples (db) and distilled water (1 : 2, w/w) added with a microsyringe to corn starch in pre-weighed aluminium sample pans. The pan was hermetically sealed and allowed to equilibrate for 12 h before analysis (Luo *et al.* 2006; Klein *et al.* 2013). The time was enough for the hydration of corn starch examples. For all DSC runs, a sealed empty aluminium pan was used as a reference. The sample was held isothermally at 20°C for 1 min before being heated from 20°C to 120°C at a rate of 10°C/minute. The onset temperature (T_o),

doi: 10.17221/125/2015-CJFS

peak temperature (T_p), conclusion temperature (T_c), and gelatinisation enthalpy (ΔH, J/g) of corn starch and starch extrudate particles were determined. The DSC measurements were performed in triplicate.

Thermogravimetric analysis (TGA). Thermal stability was determined by the method of Leblanc *et al.* (2008) with some modifications using a thermogravimetric analyser (STA 449; Netzsch, Minich, Germany). Samples weighing 3 mg (previously dried at 105°C during 1 h) were placed in the balance system and then heated from 50°C to 500°C, with a heating rate of 10°C/min under nitrogen atmosphere to prevent thermoxidative degradation. The degradation temperature was calculated using the Proteus Thermal Analysis Software.

Statistical analysis. Statistical analyses of data were conducted using the SPSS Statistics software (Version 20.0; International Business Machines Corporation, USA). Data were subjected to analysis of variance (ANOVA), and comparison of means was carried out by Duncan's multiple-range test. All determinations were performed in triplicate and mean values ± standard deviations (SD) were reported. Difference was considered to be statistically significant at $P < 0.05$. Origin 8.5 and Adobe Photoshop CS5 procedures were used to draw figures.

RESULTS AND DISCUSSION

Granular structure. The surface morphology of native corn starch and starch extrudate particles is shown in Figure 1. The native corn starch particles were polyhedral, round, and oval in shape. Corn starch extrudate particles appeared in irregular shape compared to native starch. Corn starch-CSL extrudate particles showed some small fragments on the outer layer of the starch particles. Clear fissures and grooves were observed on the surface of starch-DATEM extrudate particles. The surface of corn starch-GMS and SE extrudate particles was less flat and became rough.

The significant variations indicated changes in the surface structure of the corn starch extrudate particles. This was probably caused by the presence of native starch and emulsifier gelatiniSation during the extrusion processing (Leblanc *et al.* 2008; Bhandari *et al.* 2013; García-Tejeda *et al.* 2013; Li *et al.* 2014). These phenomena were similar to those reported by Singh *et al.* (2007). This change in granular morphology of corn starch was probably due to both high temperature and high shear, conditions that are more likely to facilitate morphological changes after extrusion processing (Da Rosa Zavareze & Dias 2011).

Swelling power (SP) and solubility (S). The swelling power and solubility of the native corn starch and corn starch extrudate particles were increased with increasing temperature from 55°C to 95°C, which is presented in Figures 2 and 3, respectively. The lower swelling power was found for corn starch extrudate particles at the same measurement temperature. These results might be due to several reasons as follows: (1) It is commonly believed that the native crystalline structure of starch was greatly disrupted

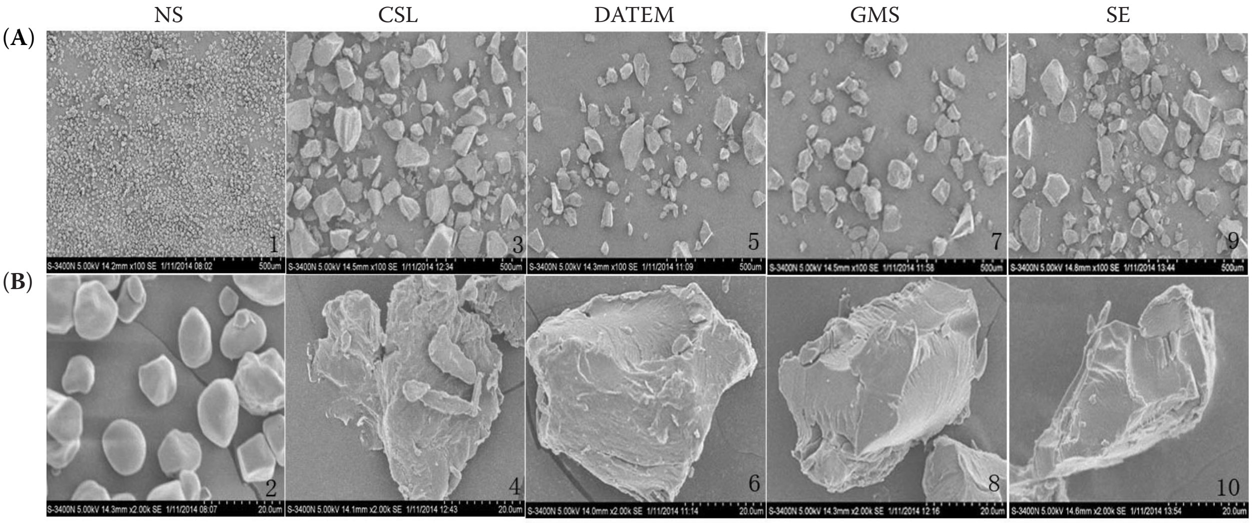

Figure 1. SEM micrographs of native corn starch (ns) and corn starch extrudate particles (3–10) at magnification 100× (A) and 2000× (B), respectively

NS – native corn starch (1, 2); CSL – starch CSL extrudate particles (3, 4); DATEM – starch DATEM extrudate particles (5, 6); GMS – starch GMS extrudate particles (7, 8); SE – starch SE extrudate particles (9, 10)

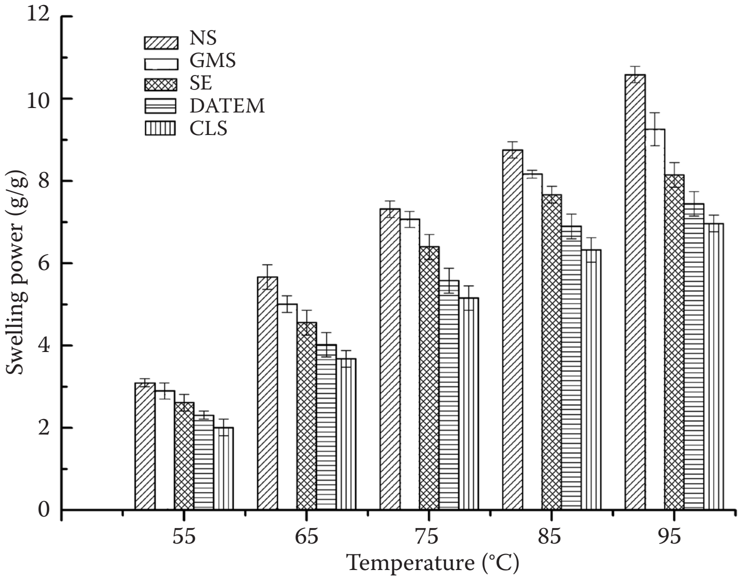

Figure 2. Swelling power of native corn starch (NS) and corn starch extruded with CSL exrudate particles (CSL), corn starch DATEM extrudate particles (DATEM), corn starch GMS extrudate particles (GMS), and corn starch SE extrudate particles (SE)

Mean values ± standard deviation (SD) of three replications

and the starch structure was degraded after extrusion processing (Li *et al.* 2014). The intermolecular hydrogen bonds of starch were broken after extrusion processing and the granular arrangement was less compact, which restricted the starch particle swelling; (2) The swelling power of the starch may be affected by the structural rearrangements of their constituent between amylose and emulsifier. The lipid and corn starch formed crosslinks between the starch chains in the amorphous and/or crystalline starch particles, which restricted starch swelling and stabilised these regions (Sun *et al.* 2014); (3) The starch was combined with the ester bond of emulsifier to form a water layer and providing steric hindrance (Dole *et al.* 2005), which restricted the swelling of starch. The swelling power of starch extrudate particles was decreased in the followed order: GMS > SE > DATEM > CSL.

The solubility of the corn starch extrudate particles was higher than that of the native corn starch. The starch DATEM extrudate particles showed the highest solubility, whereas the starch GMS extrudate particles had the lowest solubility at the same temperature. Extrusion processing caused the degradation of starch molecules and amylose content increased (Gumul *et al.* 2014; Li *et al.* 2014), which could increase the mobility of starch molecules. It was observed that amylose content was positively related to solubility (Wang *et al.* 2014), which is consistent with our results. The emulsifier has a multiple hydroxyl and ester bond and good emulsification stability, which

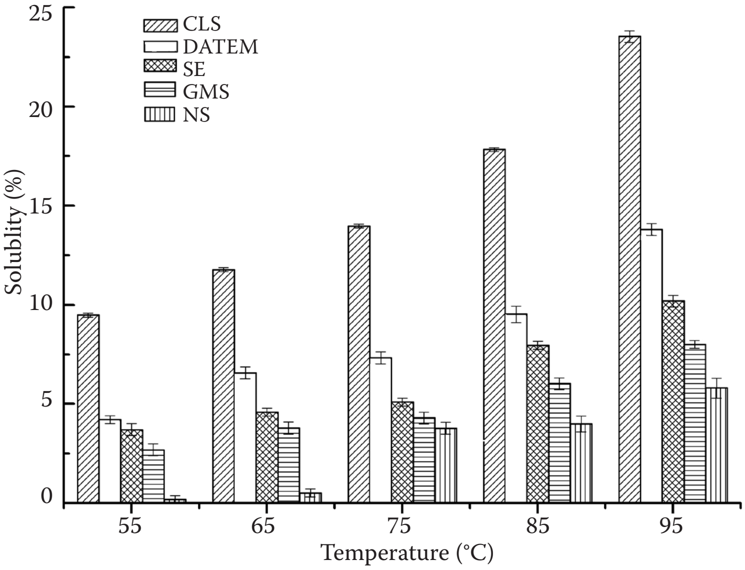

Figure 3. Solubility of native corn starch (NS) and corn starch extruded with CSL exrudate particles (CSL), corn starch DATEM extrudate particles (DATEM), corn starch GMS extrudate particles (GMS), and corn starch SE extrudate particles (SE)

Mean values ± standard deviation (SD) of three replications

Table 1. Pasting properties of corn starch and corn starch extrudate particles

Sample	Peak viscosity	Trough viscosity	Breakdown	Final viscosity	Setback	Pasting temperature (°C)
	(cP)					
NS	1250.00 ± 16.65^a	1020.00 ± 11.53^a	238.00 ± 8.14^a	1164.00 ± 18.56^a	144.00 ± 7.02^e	87.00 ± 1.78^a
CSL	474.00 ± 16.26^b	388.00 ± 11.24^b	85.00 ± 5.03^b	785.00 ± 19.86^b	396.00 ± 11.06^a	75.00 ± 2.17^b
DATEM	376.00 ± 7.09^c	299.00 ± 7.76^c	77.00 ± 1.00^c	554.00 ± 7.02^c	256.00 ± 1.52^b	68.00 ± 1.25^c
SE	310.00 ± 7.51^d	249.00 ± 7.64^d	60.00 ± 2.51^d	482.00 ± 6.51^d	233.00 ± 2.00^c	59.00 ± 0.38^d
GMS	254.00 ± 2.52^e	201.00 ± 4.50^e	53.00 ± 2.00^e	387.00 ± 10.69^e	186.00 ± 6.25^d	49.00 ± 0.75^e

All data represent the mean of three determinations; NS – native corn starch; CSL – starch CSL extrudate particles; DATEM – starch DATEM extrudate particles; SE – starch SE extrudate particles; GMS – starch GMS extrudate particles; mean ± standard deviation ($n = 3$); means with the same lower-case letter (a–e) in each column are not significantly different ($P < 0.05$); values expressed are mean± standard deviation

could improve the ability of starch combining with water. Results in this study showed that the effectiveness of emulsifiers to increase the solubility of starch is according to the order of CSL > DATEM > SE > GMS > NS. This would make corn starch extrudate particles enjoy wide technical application in food processing areas where solubility is an essential factor.

Pasting properties. The pasting properties of native corn starch and starch extrudate particles are presented in Table 1. Corn starch extrudate particles resulted in a decrease in the peak viscosity, final viscosity, trough viscosity, and breakdown. Starch extrudate particles displayed a lower peak viscosity (254–474 cP) compared with the native corn starch (1250 cP). Among the starch extrudate particles, the trough viscosity was lowest for the starch GMS extrudate particles (201 cP) while it was highest for the starch CSL extrudate particles (388 cP), which was lower than that of native corn starch (1020 cP). The FV of starch extrudate particles (387–785) was lower than in native corn starch (1164 cP). The changes in pasting characteristics indicated that starch molecules underwent some degree of reassociation during extrusion processing. These results might be due to associations between chains in the amorphous region of the particle as well as changes in the crystallinity (Da Rosa Zavareze & Dias 2011). The emulsifier then coated the starch surface, and the delayed water was transported into the starch particle (Ryu & Walker 1993; Sarawong *et al*. 2014), which might lead to the decreased viscosity of the corn starch extrudate particles. Moreover, different emulsifiers had different effects on the viscosity of the corn starch extrudate particles, which might be due to both different levels of starch degradation and different formed types of corn starch emulsifier complexes.

We found that the addition of emulsifier exhibited a significant decrease of BD, compared to native corn starch. A decrease in BD suggested that the corn starch extrudate particles were a result of disintegration of the swollen particles and leaching out of amylose molecules during extrusion processing. The lower breakdown viscosity value means greater resistance to disintegration (Meng *et al*. 2014). High extrusion temperature disrupts the starch particles, which formed an elastic fluid mass with reduced viscosity (Bisharat *et al*. 2013). A decrease in the viscosity of starch extrudate particles suggested that the degradation of starch was caused by both the attack of OH radicals and mechanochemical effects during extrusion treatment. The extent of the decrease in viscosity followed the order: CSL, DATEM, SE and GMS. In addition, the different emulsifiers affected the viscosity of corn starch in a variable manner.

X-ray powder diffraction (XRD). The X-ray powder diffraction patterns and relative crystallinity of native corn starch and corn starch extrudate particles are shown in Figure 4 and Table. 2. Diffraction patterns of the native corn starch had peaks at 2θ of 15.02, 17.02, 18.01, and 23.02°, which indicated that the native corn starch might be an A-type structure. This result is similar to Liu *et al*. (2014). Starch extrudate particles, however, exhibited a weak V-type crystal structure, as evidenced by the appearance of diffraction peaks at 2θ equal to 7.5, 13.7, and 19.6°. The weak V-type crystal structure was due to a small amount of emulsifier (1.2%) addition. The alteration of the diffraction peak of corn starch may be due to that the emulsifier and corn starch particles melted and the corn starch complexes were formed during extrusion processing (Teixeira *et al*. 2012). Corn starch combined lipid formed corn starch emulsi-

doi: 10.17221/125/2015-CJFS

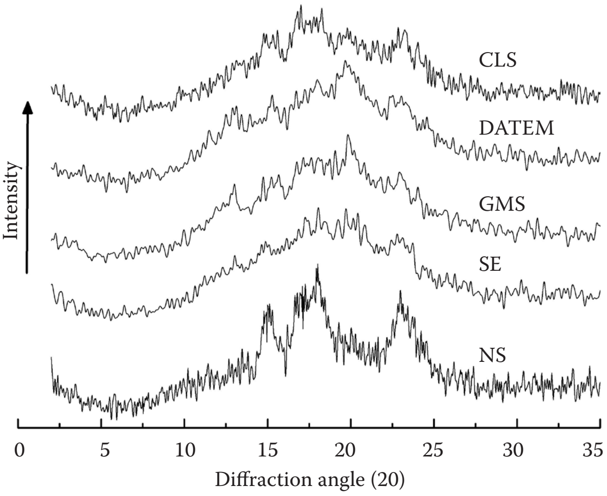

Figure 4. X-ray diffraction patterns of native corn starch (NS) and corn starch extruded with DATEM, GMS, SE, and CSL, respectively

fier complexes to produce "V" structure, which was consistent with Zhang *et al.* (2014). Compared to native starch, the relative crystallinity of starch-CSL, starch-DATEM, starch-SE, and starch-GMS complexes was decreased to 11.09, 9.91, 7.06, and 6.49%, respectively. The amorphous region of the corn starch extrudate particles was larger than that of native corn starch. This result might be due to that amylopectin double helices were dissociated to build up the crystalline lamellae and the internal parts along with the branching points are located in amorphous lamellae during the extrusion processing (Robin *et al.* 2011; Li *et al.* 2014). The rupture of starch particles might be a possible explanation for the loss of some crystallinity (Wang *et al.* 2010; Li *et al.* 2014). Different crystallinity of starch extrudate particles may be due to the combination extents between corn starch and emulsifier.

Table 2. X-ray diffraction data of native and corn starch extrudate particles

Samples	Relative crystallinity (%)	Type of diffraction pattern
NS	20.60 ± 0.32^{d}	A
CSL	11.09 ± 0.15^{c}	V
DATEM	9.91 ± 0.25^{b}	V
SE	7.06 ± 0.08^{a}	V
GMS	6.49 ± 0.20^{a}	V

Values expressed are mean ± standard deviation; NS – native corn starch; GMS – starch GMS extrudate particles; CSL – starch CSL extrudate particles; DATEM – starch DATEM extrudate particles; SE – starch SE extrudate particles; value in the same column are not significantly different ($P < 0.05$); all data represent the mean of three determinations; mean ± standard deviation ($n = 3$); means with the same lower-case letter (a–d) in each column are not significantly different ($P < 0.05$)

Differential scanning calorimetry (DSC). The results of differential scanning calorimetry (T_o, T_p, T_c, and ΔH) of the native corn starch and starch extrudate particles are shown in Table 3. Compared to the native corn starch, the onset temperature of the starch-GMS, starch-SE, starch-DATEM, and starch-CSL extrudate particles was increased by 9.18, 7.96, 6.55, and 3.41°C, respectively. The peak temperature of the starch-GMS, starch-SE, starch-DATEM, and starch-CSL extrudate particles was increased by 7.94, 7.22, 5.43, and 3.18°C, respectively. The results illustrated that the gelatinisation temperature of starch extrudate particles became higher than that of native corn starch. Extrusion weakened the crystalline structure within starch particles and the double helix unwinding after extrusion processing (Li *et al.* 2014). Emulsifier combined the unwinding of the double helix formed a different type of amylose emulsifier

Table 3. DSC results of native starch and starch extrudate particles

Samples	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
NS	64.69 ± 1.14^{e}	69.25 ± 1.17^{d}	79.07 ± 0.27^{e}	13.92 ± 0.88^{a}
GMS	73.87 ± 0.56^{a}	77.19 ± 0.22^{a}	84.4 ± 0.33^{a}	1.81 ± 0.07^{b}
SE	72.65 ± 0.30^{b}	76.47 ± 0.44^{a}	83.16 ± 0.17^{b}	0.79 ± 0.01^{c}
DATEM	71.24 ± 0.21^{c}	74.68 ± 0.38^{b}	82.28 ± 0.17^{c}	0.62 ± 0.07c
CSL	68.10 ± 0.22^{d}	72.43 ± 1.35^{c}	80.71 ± 0.15^{d}	0.52 ± 0.01^{c}
CSL	68.10 ± 0.22^{d}	72.43 ± 1.35^{c}	80.71 ± 0.15^{d}	0.52 ± 0.01^{c}

NS – native starch; GMS – corn starch GMS extrudate particles; SE – corn starch SE extrudate particles; DATEM – corn starch DATEM extrudate particles; CSL – corn starch CSL extrudate particles; all data represent the mean of three determinations; mean ± standard deviation ($n = 3$); means with the same lower-case letter (a–e) in each column are not significantly different ($P < 0.05$)

doi: 10.17221/125/2015-CJFS

complexes and then reaggregation occurred, which caused a different rise in gelatinisation temperature (Bhatnagar & Hanna 1994; Luo *et al.* 2006; Li *et al.* 2014). The increased gelatinisation temperature was attributed to structural changes within the starch particles, which involved amylose–amylose and amylase–lipid interactions (Da Rosa Zavareze & Dias 2011). The higher gelatinisation temperature of starch extrudate particles was due to the reaggrangement of polymer chains into more stable configurations (Spier *et al.* 2013). The different gelatinization temperature rise may be due to that corn starch and emulsifiers formed complexes of different type. In this study, it could illustrate that the gelatinisation temperature of starch extrudate particles was in the following order: GMS > SE > DATEM > CSL.

The gelatinisation enthalpy of starch extrudate particles ranged from 0.52 J/g to 1.81 J/g. However, the gelatinisation enthalpy (ΔH) of the starch extrudate particles drastically decreased relative to the native corn starch (13.92 J/g). These values are in agreement with De Pilli *et al.* (2011), which might be due to the reactive groups introduced into the starch chains that are capable of disrupting the inter- and intramolecular hydrogen bonding (Singh *et al.* 2007). The lower gelatinisation enthalpy showed that the internal crystalline and amorphous regions of starch were destroyed and some portion of the internal double helical structure disappeared (Hu *et al.* 2014). Luo *et al.* (2006) showed that ΔH values of gelatinisation primarily reflect the loss of the ordered double helices. Hence, the starch extrudate particles would be more mobile and more prone to disruption than native corn starch. A different decrease in gelatinisation enthalpy was supposed to be different complex abilities between the starch and different emulsifiers. This would then explain a different extent of decrease in ΔH that differed between the starch extrudate particles (GMS > SE > DATEM > CSL).

Thermal gravimetric analysis (TGA). Thermogravimetric analysis curves of native corn starch and starch extrudate particles are shown in Figure 5. Thermogravimetric analysis was used to examine the changes in thermal stability between the corn starch and emulsifier. The main decomposition of starch was in three steps: one was water evaporation, and the other two corresponded to the decomposition of starch (Heinze *et al.* 2004; Mathew & Abraham 2007; Wang *et al.* 2010). The native corn starch and starch extrudate particles displayed a weight loss of water evaporation at around 100°C. The second degradation temperature of native corn starch was 270–325°C, which was lower than that of starch extrudate particles (296–356). At 500°C, the mass loss of the starch extrudates (from 82.08% to 91.75%) was lower than that of the native corn starch (97.25%). The remaining residue and the temperature of maximum decomposition of starch extrudate particles were higher than those of native corn starch. The results showed that the starch extrudate particles were found to be more thermally stable than native corn starch. The emulsifier was a coupling agent that improved the compatibility between the hydroxyl of starch and the ester bond of emulsifiers and then the thermal stability of starch extrudate particles improved (Liu *et al.* 2013; Tupa *et al.* 2015). The results clearly illustrated that the emulsifier significantly enhanced the thermal stability during extrusion processing. The thermal stability was increased to a maximum extent with GMS and to a minimum extent with CSL, while SE and DATEM showed the values in between.

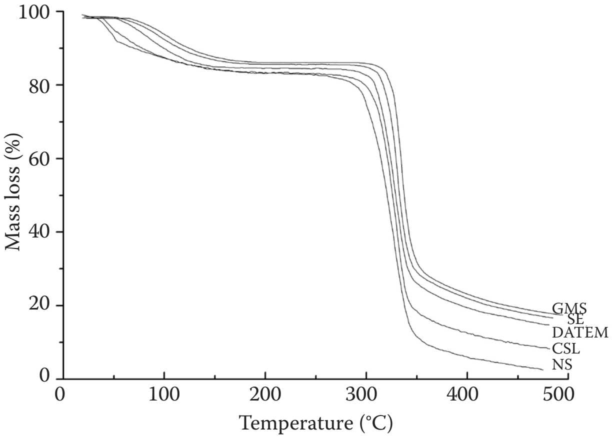

Figure 5. Thermogravimetric (TG) curves of corn starch (NS) and corn starch 561 extruded with DATEM, GMS, SE, and CSL, respectively

CONCLUSION

The present study offered a better understanding of the role of emulsifier and starch granules in the overall physicochemical properties of starch extrudate particles. Extrusion treatment decreased the crystallinity and the corn starch emulsifier complexes were formed. The emulsifier played a major role in determining the structure (XRD and SEM) of the mixtures due to their different emulsifying capacity. The amorphous part of corn starch was increased and

doi: 10.17221/125/2015-CJFS

the diffraction pattern changed the crystal structure from A-type to V-type. The increasing thermal stability and solubility depended not only on the crystal structure, but also on the dissociated and restructured starch structure. It was concluded that the sizes of corn starch extrudate particles were not uniform and the shape varied. The information obtained from this study may provide useful insights into the formulation of the improved thermal stability and solubility of starch extrudate particles in the food processing area.

References

Ali T.M., Hasnain A. (2013): Effect of emulsifiers on complexation and functional properties of oxidized white sorghum (*Sorghum bicolor*) starch. Journal of Cereal Science, 57: 107–114.

Azizi M.H., Rao G.V. (2005): Effect of surfactant in pasting characteristics of various starches. Food Hydrocolloids, 19: 739–743.

Bhandari P.N., Jones D.D., Hanna M.A. (2013): Characterization of sodium starch glycolate prepared using reactive extrusion and its comparisons with a commercial brand VIVASTAR®P. Industrial Crops and Products, 41: 324–330.

Bhatnagar S., Hanna M.A. (1994): Amylose-lipid complex formation during single-screw extrusion of various corn starches. Cereal Chemistry, 71: 582–587.

Bisharat G.I., Oikonomopoulou V.P., Panagiotou N.M., Krokida M.K., Maroulis Z.B. (2013): Effect of extrusion conditions on the structural properties of corn extrudates enriched with dehydrated vegetables. Food Research International, 53: 1–14.

Carrillo-Navas H., Pérez-Alonso C., Fouconnier B., Vernon-Carter E.J., Alvarez-Ramírez J. (2014): Inertial effects of adsorbed glycerol monostearate crystals on the shear rheology of water/canola oil interfaces. Journal of Food Engineering, 125:112–118.

Choi S.G., Kerr W.L. (2003): Effects of chemical modification of wheat starch on molecular mobility as studied by pulsed 1H NMR. LWT-Food Science and Technology, 36: 105–112.

Conde-Petit B., Escher F. (1995): Complexation induced changes of rheological properties of starch systems at different moisture levels. Journal of Rheology, 39: 1497–1518.

da Rosa Zavareze E., Dias A.R.G. (2011): Impact of heat-moisture treatment and annealing in starches: a review. Carbohydrate Polymers, 83: 317–328.

De Pilli T., Carbone B.F., Fiore A.G., Severini C. (2007): Effect of some emulsifiers on the structure of extrudates with high content of fat. Journal of Food Engineering, 79: 1351–1358.

De Pilli T., Derossi A., Talja R.A., Jouppila K., Severini C. (2011): Study of starch-lipid complexation in model system and real food produced using extrusion-cooking technology. Innovative Food Science & Emerging Technologies, 12: 610–616.

Dole P., Avérous, L., Joly C., Valle G.D., Bliard C. (2005): Evaluation of starch-PE multilayers: processing and properties. Polymer Engineering & Science, 45: 217–224.

Galloway G.I., Biliaderis C.G., Stanley D.W. (1989): Properties and structure of amylose-glyceryl monostearate complexes formed in solution or on extrusion of wheat flour. Journal of Food Science, 54: 950–957.

García-Tejeda Y.V., López-González C., Pérez-Orozco J.P., Rendón-Villalobos R., Jiménez-Pérez A., Flores-Huicochea E., Solorza-Feria J., Bastida C.A. (2013): Physicochemical and mechanical properties of extruded laminates from native and oxidized banana starch during storage. LWT-Food Science and Technology, 54: 447–455.

Gomes-Ruffi C.R., Da Cunha R.H., Almeida E.L., Chang Y.K., Steel C.J. (2012): Effect of the emulsifier sodium stearoyl lactylate and of the enzyme maltogenic amylase on the quality of pan bread during storage. LWT-Food Science Technology, 49: 96–101.

Gumul D., Krystyjan M., Buksa K., Ziobro R., Zięba T. (2014): The influence of oxidation, extrusion and oxidation/extrusion on physico-chemical properties of potato starch. Starch/Stärke, 66: 190–198.

Heinze T., Liebert T., Heinze U., Schwikal K. (2004): Starch derivatives of high degree of functionalization 9: Carboxymethyl starches. Cellulose, 11: 239–245.

Hu A.j., Li L., Zheng J., Lu J., Meng X., Liu Y., Rehman R.U. (2014): Different-frequency ultrasonic effects on properties and structure of corn starch. Journal of the Science of Food and Agriculture, 94: 2929–2934.

Klein B., Pinto V.Z., Vanier N.L., da Rosa Zavareze E., Colussi R., do Evangelho J.A., Gutkoski L.C., Dias A.R.G. (2013): Effect of single and dual heat-moisture treatments on properties of rice, cassava, and pinhao starches. Carbohydrate Polymers, 98: 1578–1584.

Krog N. (1973): Influence of food emulsifiers on pasting temperature and viscosity of various starches. Starch/Stärke, 25: 22–27.

Lazou A., Krokida M. (2010): Structural and textural characterization of corn-lentil extruded snacks. Journal of Food Engineering, 100: 392–408.

Leblanc N., Saiah R., Beucher E., Gattin R., Castandet M., Saiter J.M. (2008): Structural investigation and thermal stability of new extruded wheat flour based polymeric materials. Carbohydrate Polymers, 73: 548–557.

Li M., Hasjim J., Xie F.W., Halley P.J., Gilbert R.G. (2014): Shear degradation of molecular, crystalline, and granular structures of starch during extrusion. Starch/Stärke, 66: 595–605.

doi: 10.17221/125/2015-CJFS

Liu X.X., Wang Y.F., Yu L., Tong Z., Chen L., Liu H.S., Li X.X. (2013): Thermal degradation and stability of starch under different processing conditions. Starch/Stärke, 65: 48–60.

Liu J.H., Wang B., Lin L., Zhang J.Y., Liu W.L., Xie J.H., Ding Y.T (2014): Functional, physicochemical properties and structure of cross-linked oxidized maize starch. Food Hydrocolloids, 36: 45–52.

Luo Z.G., He X.W., Fu X., Luo F.X., Gao Q.Y. (2006): Effect of microwave radiation on the physicochemical properties of normal corn, waxy corn and amylocorn V starches. Starch/Stärke, 58: 468–474.

Martinez M.M., Calviño A., Rosell C.M., Gómez M. (2014): Effect of different extrusion treatments and particle size distribution on the physicochemical properties of rice flour. Food and Bioprocess Technology, 7: 2657–2665.

Mathew S., Abraham T.E. (2007): Physico-chemical characterization of starch ferulates of different degrees of substitution. Food Chemistry, 105: 579–589.

Meng Y.C., Sun M.H., Fang S., Chen J., Li Y.H. (2014): Effect of sucrose fatty acid esters on pasting, rheological properties and freezeethaw stability of rice flour. Food Hydrocolloids, 40: 64–70.

Miao M., Jiang B., Zhang T. (2009): Effect of pullulanase debranching and recrystallization on structure and digestibility of waxy maize starch. Carbohydrate Polymers, 76: 214–221.

Moad G. (2011): Chemical modification of starch by reactive extrusion. Progress in Polymer Science, 36: 218–237.

Ponzio N.R., Ferrero C., Puppo M.C. (2013): Wheat varietal flours: influence of pectin and DATEM on dough and bread quality. International Journal of Food Properties, 16: 33–44.

Robin F., Théoduloz C., Gianfrancesco A., Pineau N., Schuchmann H.P., Palzer S. (2011): Starch transformation in bran-enriched extruded wheat flour. Carbohydrate Polymers, 85: 65–74.

Ryu G.H., Walker C.E. (1993): Emulsifier effects on pasting properties of wheat flour extrudates with/without sucrose and shortening. Strarch/Stärke, 45: 65–70.

Sarawong C., Schoenlechner R., Sekiguchi K., Berghofer E., Ng P.K.W. (2014): Effect of extrusion cooking on the physicochemical properties, resistant starch, phenolic content and antioxidant capacities of green banana flour. Food Chemistry, 143: 33–39.

Singh J., Kaur L., McCarthy O.J. (2007): Factors influencing the physico-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications – a review. Food Hydrocolloids, 21: 1–22.

Singh N., Cairns P., Morris V.J., Smith A.C. (1998): Physical properties of extruded wheat starch-additive mixtures. Cereal Chemistry, 75: 325–330.

Spier F., Zavareze E.D.R., Marques e Silva R., Elias M.C., Dias A.R.G (2013): Effect of alkali and oxidative treatments on the physicochemical, pasting, thermal and morphological properties of corn starch. Journal of the Science of Food and Agriculture, 93: 2331–2337.

Sun Q. J., Dai L., Nan C., Xiong L. (2014): Effect of heat moisture treatment on physicochemical and morphological properties of wheat starch and xylitol mixture. Food Chemistry, 143: 54–59.

Szűts A., Szabó-Révész P. (2012): Sucrose esters as natural surfactants in drug delivery systems – a mini review. International Journal of Pharmaceutics, 433: 1–9.

Teixeira E.D.M., Curvelo A.A.S., Corrêa A.C., Marconcini J.M., Glenn G.M., Mattoso L.H. (2012): Properties of thermoplastic starch from cassava bagasse and cassava starch and their blends with poly (lactic acid). Industrial Crops and Products, 37: 61–68.

Tupa M.V., Ramírez J.A.Á., Vázquez A., Foresti M.L. (2015): Organocatalytic acetylation of starch: effect of reaction conditions on DS and characterisation of esterified granules. Food Chemistry, 170: 295–302.

Wang L.F., Pan S.Y., Hu H., Miao W.H., Xu X.Y. (2010): Synthesis and properties of carboxymethyl kudzu root starch. Carbohydrate Polymers, 80: 174–179.

Wang N., Warkentin T.D., Vandenberg B., Bing D.J. (2014): Physicochemical properties of starches from various pea and lentil varieties, and characteristics of their noodles prepared by high temperature extrusion. Food Research International, 55: 119–127.

Yu L., Ramaswamy H.S., Boye J. (2012): Twin-screw extrusion of corn flour and soy protein isolate (SPI) blends: A response surface analysis. Food and Bioprocess Technology, 5: 485–497.

Zhang L.M., Cai W.T., Shan J., Zhang S., Dong F. (2014):. Physical properties and loading capacity of gelatinized granular starches. Industrial Crops and Products, 53: 323–329.

Zhang Y., Huang L., Zhou H.B., Zhang P.P., Zhu M., Fan B.B., Wu Q.X. (2013): Tough thermoplastic starch modified with polyurethane microparticles by reactive extrusion. Starch/Stärke, 65: 425–432.

Received: 2015–03–12
Accepted after corrections: 2015–08–05

Corresponding author:
Prof Zhigang Xiao, Northeast Agricultural University, College of Food Science, No. 59 Mucai Street Xiangfang District Harbin 161006, P.R. China; E-mail: synu_xzg66@126.com