

The effects of defatting and heat–moisture treatment on the retrogradation of starch gels from wheat, oat, potato, and lentil

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Abstract

During storage of defatted and heat–moisture treated starch gels, the results of this work show that the magnitude of interaction between starch chains in the amylose matrix (continuous phase) and within gelatinized granules (dispersed phase), is influenced to a large extent by the interplay of the changes (on defatting and heat–moisture treatment) in crystallinity, swelling factor, and amylose leaching, and by the chain length of amylose and amylopectin.

1. Introduction

Lipids associated with cereal, legume, root, and tuber starch granules have been found to occur on the surface as well as inside the granule [1]. The surface lipids [1–3] are mainly triglycerides, followed by free fatty acids, glycolipids, and phospholipids. The internal lipids [1,3,4] are predominantly monoacyl lipids, with the major components being lysophospholipids and free fatty acids.

Starch lipids are known to occur in the free state as well as bound to starch components, either linked via ionic or by hydrogen bonding to the hydroxyl groups of the starch components, or with the formation of amylose-inclusion complexes in which the ligand resides within the central hydrophobic core of the helix [1,5]. The formation of amylose–lipid complexes have also been shown to occur during gelatinization [2,6]. However, controversy still exists with regard to the interaction

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of native lipids with amylopectin [1–11]. Huang and White [11] showed recently that addition of monoglycerides to waxy corn starch reduces the crystallization of amylopectin during storage.

The effect of defatting on swelling power (SP), solubility, crystallinity, pasting properties, and gelatinization transition temperatures have been studied by several researchers. Lorenz [12] reported that defatting with 80% methanol increased the SP and solubility of wheat starch, whereas in potato starch, the SP remained unchanged while the solubility decreased. Goshima et al. [13] reported that the SP and solubility of potato starch increased on defatting with 99% methanol. Tester and Morrison [14] reported that partial extraction of lipids from wheat starch with anhydrous methanol at 100°C increased the swelling factor by 30%. Recently we showed [15,16] that defatting of wheat, corn, oat, lentil, potato, and oat starches with hot 3:1 1-propanol–water (PW) decreased the swelling factor of all starches. Whereas, amylose leaching decreased [15,16] on defatting in potato, cassava, and lentil starches but increased in wheat [15], corn [15], and oat [16] starches.

Lorenz [17] reported that lipid removal (0.54–0.61%) from wheat starch with 80% methanol did not affect the peak viscosity at 92°C. Melvin [18] reported that lipid removal (0.4–0.5%) from corn and wheat starches by slurring at 70°C with water-saturated 1-butanol (5 h) or by Soxhlet extraction using 85% aqueous methanol (72 h) decreased the pasting temperature but increased the pasting peak and paste consistencies. Takahashi and Seib [19], however, showed that lipid removal from wheat (1.00%) and corn (0.82%) starches with boiling 75% ethanol eliminated the pasting peak, reduced consistency, and set-back and decreased the pasting temperature. Lorenz [12] showed that lipid removal from potato starch with 80% methanol (48 h) did not significantly alter the amylograph consistencies. Goshima et al. [13], however, reported that lipid removal (0.064%) from potato starch with 99% methanol (15 h) in a Soxhlet extractor reduced the pasting temperature, increased paste consistency at 67.8°C, and caused no change in thermal stability during the holding period. Vasanthan and Hoover [15] showed that defatting of wheat, corn, oat, potato, and lentil starches with PW (results in almost complete removal of lipids) eliminated the pasting peak of the cereal starches and increased the thermal stability and reduced the hot paste consistency of all starches.

Lorenz [12] observed that wheat and potato starches showed no changes in their X-ray pattern on defatting with 80% methanol for 48 h. Furthermore, defatting was shown to cause a decrease in relative crystallinity (RC), which amounted to 1.7 and 6.8% in potato and wheat starch, respectively. Vasanthan and Hoover [15] reported that defatting with PW increased the RC of potato and lentil starches by 21 and 7.8% respectively, while those of wheat, corn, and cassava starches remained virtually unchanged.

Takahashi and Seib [19] showed that extraction of wheat and corn starches with 75% ethanol did not cause any significant changes in their gelatinization temperature. Similar observations were made by Lorenz [12] (80% methanol) and Goshima et al. [13] (99% methanol) on wheat and potato starches respectively. Defatting with PW [15] was found to increase the gelatinization temperatures of potato and

lentil starches, but did not significantly affect those of wheat, corn, and cassava starches.

Vasanthan and Hoover [15] have shown that the changes in starch granule structure and physicochemical properties on defatting depends on the type of crystalline structure (A, B, or C), nature, and composition of the extracting solvent system, maximum temperature experienced by the starch granules, extent of association between amylose and amylopectin chains in the native granule, and on the lipid content.

Heat-treatment of cereal, tuber, and legumes starches at low water contents (18–27%) and high temperature (100°C) for 16 h has been shown [20–32] to increase the paste stability, shear stability and gelatinization temperatures and decrease the SP and solubility. The susceptibility towards alpha-amylase increases on heat–moisture treatment in potato [11,31], yam [31], and pigeon pea starches [32], but decreases in wheat [31] and lentil [31] starches. Heat-moisture treatment increases the X-ray diffraction intensities of wheat, oat, and lentil starches [31], but decreases those of potato and yam starches [31]. In cereal starches, X-ray patterns remain unchanged on heat–moisture treatment [23,26,31], whereas in tuber [25,31] and lentil [31] starches they become more cereal-like. The gelatinization enthalpy [31] of wheat, oat, and lentil starches remain unchanged, but those of potato and yam starches decrease on heat–moisture treatment. Hoover and Vasanthan [31] have shown that the extent of starch-chain associations within the amorphous regions, and the degrees of crystalline order are altered during heat–moisture treatment. The magnitude of these changes are dependent upon the moisture content during heat treatment and on the starch source.

When heated, an aqueous suspension of starch granules undergoes an order–disorder transition known as gelatinization. The starch chains become hydrated, granules swell, amylose is leached out, and birefringence and crystallinity disappears. Slade and Levine [33] have postulated that crystallite melting during gelatinization is indirectly controlled by the kinetically constrained continuous amorphous surroundings. That is, melting of microcrystallites, which are highly hydrated clusters of amylopectin branching, is controlled by prerequisite plasticization of the amorphous regions of the granule. On cooling, gelatinized starch suspensions begin to retrograde. Retrogradation is accompanied by increases in the degree of crystallinity, gel firmness, turbidity, and the appearance of a 'B' X-ray diffraction pattern [34]. Studies on the retrogradation of starch gels [35] using X-ray diffraction, differential scanning calorimetry, and shear modulus, have shown that the short term development of gel structure and crystallinity in starch gels, is dominated by irreversible ($T < 100^{\circ}\text{C}$) gelation and crystallization within the amylose matrix, whereas long-term increases in the modulus of starch gels were linked to a reversible crystallization (within gelatinized granules) involving amylopectin. It was postulated [35] that crystallization resulted in an increase in the rigidity of the granules and thus, enhanced their reinforcement of the amylose matrix.

The retrogradation of starches from wheat [36,37], maize [38,39], waxy maize [39–42], potato [36,38,43], rice [44,45], and pea starches [38] have been subjected to

detailed study. However, there is a dearth of information on the influence of defatting and heat–moisture treatment on the extent of retrogradation of starches from different plant origins. Recently, we showed that defatting [15] with 3:1 1-propanol–water causes interactions to occur between amylopectin chain clusters. This was found to be more pronounced in potato and lentil than in wheat and oat starches. Heat-moisture treatment treatment [31] was found to favor interactions between starch chains within the amorphous regions of the granule and to cause changes in the packing arrangement of starch crystallites of wheat, oat, potato, and lentil starches. Furthermore, crystallite disruption was found to occur during heat–moisture treatment [31] in potato starch, but not in wheat, oat, and lentil starches. The aim of this investigation was to determine how the foregoing structural changes during defatting and heat–moisture treatment, influence the crystallization mechanism during storage of concentrated wheat, oat, potato, and lentil starch gels at ambient temperatures.

2. Experimental

Materials. — Wheat and potato starches were obtained from Sigma Chemical Co., St. Louis, MO, USA, Seeds of lentil (*Lens culinaris Medicus*) were obtained from a local supplier. AC Hill oat grains (*Avena nuda*, var *chinensis*. Fish. ex link) which is a spring type, day length-sensitive cultivar were obtained from the central experimental farm at Ottawa. The extraction of lentil and AC Hill oat starches were carried out by procedures outlined in earlier publications [46,47].

Chemical composition of starch. — Quantitative estimations of moisture, ash, starch damage, and nitrogen were performed by the standard AACC [48] procedures. Starch lipids were analyzed as follows: at ambient temperatures (25–27°C) lipids were extracted from starches (5 g dry basis) with 100 ml of 2:1 CHCl₃–MeOH under vigorous agitation in a wrist action shaker for 1 h. At elevated temperatures (90–100°C) lipids were obtained by Soxhlet extraction (7 h) with 100 mL of 3:1 1-propanol–water. Lipids were also extracted, after acid hydrolysis of starches with 24% HCl for 30 min at 70–80°C and the hydrolyzate then extracted three times with 1-hexane [13]. The purification and quantification of lipids were carried out by procedures that have been described elsewhere [3]. Apparent and total amylose content was determined by the method of Chrastil [49].

Heat–moisture treatment. — The method of heat–moisture treatment was that of Sair [22], with minor modifications. Starch samples (15 g dry basis) were weighed into glass containers. Starch moisture content was brought to 30% by adding the appropriate amount of distilled water. The starch samples were mixed thoroughly during the addition of water. The containers were sealed, kept for 24 h at ambient temperature, and then placed in a forced-air oven for 16 h at 100°C. Afterwards the containers were opened, and the starch samples air dried to a uniform moisture content (~10%).

Swelling factor. — The swelling factor (SF) of the starches when heated to 95°C in excess water was measured according to the method of Tester and Morrison

[14]. This method measures only intragranular water and hence the true SF at a given temperature. The SF is reported as a ratio of the volume of swollen starch granules to the volume of the dry starch.

Extent of amylose leaching. — Various concentrations of native and treated starches (15–20 mg) in water (15–20 mL) were heated (95°C) in volume-calibrated sealed tubes for 30 min. The tubes were then cooled to ambient temperature and centrifuged at 3600 rpm for 10 min. The supernatant liquid (1 mL) was withdrawn and its amylose content was determined by the method of Chrastil [49].

Gel preparation. — Gels (40% w/v) were prepared as described by Krusi and Neukom [50]. Native, defatted, and heat-moisture treated starch samples (4 g dry basis) were carefully weighed into circular aluminum moulds (diameter 3.0 cm, height 3.0 cm) with removable tops and bases and then mixed with 10 mL of distilled water containing 0.02% $\text{Na}_2\text{S}_2\text{O}_3$ as preservative. The moulds were then heated in a water bath at for 30 min. at 25°C. The resulting gels were allowed to cool within the moulds for 30 min at 4°C prior to storage for 24 h at 25°C.

Gel texture determination. — The resistance to penetration of the gel during storage at 25°C was determined with a model 6000 R Lloyd texture testing machine (Omnitronix Instruments Ltd., Mississauga, ON, Canada) equipped with a data acquisition and processing station (Lloyds Instruments Inc.). The 5 and 50 N load cells were used. The gels within the aluminum moulds were placed on the compression table. The load cell was fitted to the cross beam, and driven down so as just to touch the gel surface. The cylindrical probe (5-mm diameter) was then driven at a constant speed (0.5 mm/min) into the gel for a distance of 6 mm. The

Table 1
Proximate composition of native starches

Characteristics	Composition (%) ^a			
	Wheat	Oat	Lentil	Potato
Moisture	9.9	9.4	9.6	9.7
Ash	0.02	0.03	0.03	0.05
Nitrogen	0.04	0.05	0.02	0.03
Starch damage	0.8	1.3	0.6	1.2
Lipid(solvent extracted)				
Chloroform-methanol [CM] ^b	0.04	0.07	0.03	0.02
Propanol-water [PW] ^c	0.64	1.05	0.11	0.09
Acid hydrolysed ^d	0.70	1.13	0.14	0.11
Amylose content (% of total starch)	21.1	16.7	36.7	21.0
Apparent ^e				
Total ^e	27.3	19.4	38.0	24.7

^a All data reported on dry basis, and represent the mean of three determinations.

^b Lipids extracted from native starch by 2:1 CM at 25°C (mainly unbound lipids).

^c Lipids extracted by hot 3:1 PW from the residue left after CM extraction (mainly bound lipids).

^d Lipids obtained by acid hydrolysis (24% HCL) of the native starch (total lipids).

^e Apparent and total amylose determined by I_2 -binding before, and after removal of bound lipids by hot PW extraction.

load at 1-mm compression was termed firmness. The resulting readings were in units of load grams.

Differential scanning calorimetry (DSC). — Gelatinization temperatures were measured and recorded on a Perkin–Elmer DSC-2 (Norwalk, CT) differential scanning calorimeter, equipped with a thermal analysis data station. Water (8.0 μ L) was added with a microsyringe to starch (2.5 mg dry basis) in the DSC pans, which were then sealed, reweighed, and kept overnight at room temperature. The scanning temperature range and the heating rate were 20–120°C and 10°C/min, respectively. The thermogram was recorded with water as reference.

The transition temperatures reported are the onset (T_0), peak (T_p), and conclusion (T_c) of the gelatinization endotherm. Indium was used for calibration. The enthalpy of gelatinization (ΔH) was estimated by integrating the area between the thermogram and a base line under the peak, and was expressed in terms of joules per unit weight of dry starch (J/g).

Fusion of retrograded amylopectin at various time intervals of storage (0.5 h–20 days), was determined by weighing (3–4 mg dry basis) of the stored (at 25°C) gels (40% w/v) into DSC pans which were then sealed and scanned from 20 to 100°C at 5°C/min. All DSC experiments were replicated at least twice.

3. Results and discussion

Proximate composition. — The proximate analyses of the starches are presented in Table 1. All starches were of very high purity (< 0.05% nitrogen), indicating the absence of endosperm proteins and by implication, most of the non-starch lipids [1]. In all starches, the nitrogen content and the extent of starch damage were only marginally affected by defatting and heat–moisture treatment.

Differential scanning calorimetry. — The gelatinization transition temperatures (T_0 , T_p , and T_c) and the gelatinization enthalpy (ΔH) of native, defatted, and heat–moisture treated starches are presented in Table 2. The T_0 , T_p , T_c and ΔH_R representing the fusion of retrograded amylopectin (of the above starches) at various time intervals (0.5 h to 20 days) of storage (25°C) are presented in Table 3.

Defatting did not significantly affect T_0 , T_p , T_c , and the gelatinization transition range ($T_c - T_0$) of wheat and oat starches. However, defatted granules of potato and lentil gelatinized over a broader and higher temperature range than did the corresponding untreated starches (Table 2). The ΔH of all starches showed a slight increase on defatting (Table 2). These results suggest that defatting increases the degree of order within granules of potato and lentil starches [15].

As seen in Table 2, T_0 , T_p , T_c , and T_c of all starches increased on heat–moisture treatment. This reflects a decrease in the destabilization effect of the amorphous regions on the melting of starch crystallites during gelatinization [31]. Our earlier studies [31] showed that crystallites of potato starch are disrupted on heat–moisture treatment. Consequently, if changes in crystalline stability were a factor influencing increases in thermal transition temperatures during heat–moisture treatment, then T_0 , T_p , and T_c of heat–moisture treated potato starch

Table 2
Thermal characteristics of native, and treated starches

Starch source and treatment	Transition temperatures (°C) ^{abc}			Range (°C) T _c – T ₀	Enthalpy (J/g) ^d ΔH
	T ₀	T _p	T _c		
Wheat					
Native	57.0	62.0	67.0	10.0	9.7
Defatted	55.1	60.0	65.2	10.1	10.1
Heat–moisture treated	65.0	70.0	78.0	13.0	9.5
Oat					
Native	60.0	66.0	71.0	11.0	11.5
Defatted	58.0	64.0	70.0	12.0	12.2
Heat–moisture treated	64.0	75.0	80.0	16.0	11.1
Lentil					
Native	55.0	61.0	68.0	13.0	7.6
Defatted	60.3	67.0	75.1	14.8	8.0
Heat–moisture treated	64.0	71.0	78.0	14.0	7.6
Potato					
Native	54.0	59.0	64.0	10.0	16.4
Defatted	59.2	65.0	72.0	13.4	16.6
Heat–moisture treated	65.0	71.0	80.0	15.0	10.9

^a Average standard deviation 0.1 (n = 3).

^b Water:starch ratio, 3:1.

^c T_0 , T_p , and T_c indicate the temperatures of the onset, mid point, and end of gelatinization, respectively.

^d Enthalpy of gelatinization.

should have been less than that of its native counterpart. The results on potato starch, therefore, suggest that as in wheat, oat, and lentil starches, the increase in T_0 , T_p and T_c on heat-moisture treatment reflects starch-chain interactions within amorphous regions of the granule. The foregoing increases are higher in potato starch due to its longer amylose chain length [51].

The lack of influence of heat-moisture treatment on ΔH of wheat, oat, and lentil starches (Table 2), suggests that double helices do not disrupt (do not unravel) under the conditions prevailing during heat-moisture treatment. This implies that identical amounts of double helices unravel and melt during gelatinization of native and heat-moisture treated wheat, oat, and lentil starches. The decrease in ΔH on heat-moisture treatment of potato starch, suggests that some of the original double helices may have disrupted during the polymorphic transformation ('B' to 'A' + 'B').

The retrogradation endotherm of untreated starches appeared after 3 days storage in wheat, potato, and lentil starches (Table 3), whereas for oat starch, the corresponding time was 15 days (Table 3). Defatting, and heat-moisture treatment did not hasten or delay the onset time of the retrogradation endotherm in wheat, potato, and lentil starches. However, the retrogradation endotherm of defatted, and heat-moisture treated oat starches appeared after 3 and 6 days storage,

Table 3
Thermal characteristics of native, and treated starch gels ^a

Starch source and treatment	Enthalpy (ΔH_R , J/g) ^{b,c}							Transition temperatures ^{b,d} (°C)		
	Storage time (days)							T_0	T_p	T_c
	2	3	4	6	8	15	20			
Wheat										
Native		0.9	1.8	3.9	5.3	7.1	7.1	47.5	57.2	60.7
Defatted	2.0	2.6	4.0	5.3	7.3	11.0	11.8	47.1	57.9	60.4
Heat-moisture treated		2.4	3.4	5.0	6.9	9.0	9.7	46.9	58.1	59.8
Oat										
Native						1.3	1.9	46.8	57.6	60.9
Defatted		1.0	1.8	2.5	2.7	3.8	5.5	47.1	57.9	60.4
Heat-moisture treated				1.9	2.2	2.5	3.5	48.0	57.4	60.3
Lentil										
Native		0.6	1.3	2.5	3.4	6.0	8.4	47.1	57.9	62.8
Defatted		1.2	2.5	3.8	4.3	8.4	10.1	47.4	57.9	63.2
Heat-moisture treated		1.7	3.4	5.4	6.8	11.3	12.2	46.8	57.5	63.3
Potato										
Native		1.0	2.4	6.0	7.5	9.8	11.2	50.6	57.2	69.2
Defatted		1.8	3.8	8.0	10.0	12.6	13.4	50.3	58.4	69.5
Heat-moisture treated		0.8	1.9	4.7	5.7	9.1	9.7	50.5	59.1	69.1

^a Starch:water, 40:60 (w/w, dry basis).

^b All data represent the means of three determinations.

^c Average standard deviation, 0.5 J/g.

^d Average standard deviation, 0.5°C.

respectively (Table 3). The differences in T_0 , T_p and T_c of the retrogradation endotherm of native and treated starch gels were only marginal, and remained practically unchanged during the time course of retrogradation (Table 3). Furthermore, T_0 , T_p and T_c of retrograded native, and treated (Table 3) starch gels were lower than those for the gelatinization endotherm (Table 2). In native and treated starch gels, the transition temperature range ($T_c - T_0$) of the retrogradation endotherm was broader (Table 3) than that of the gelatinization endotherm (Table 2). This was most pronounced in potato starch. Unlike T_0 , T_p and T_c , the retrogradation enthalpy (ΔH_R) was greatly influenced by the type of treatment (Table 3). After 20 days storage, the ΔH_R (J/g) of gels from native starches were: 7.1 (wheat), 1.9 (oat), 8.4 (lentil), and 11.2 (potato). These values increased respectively, by 4.7, 3.6, 1.7, and 2.2 J/g on defatting. However, during the corresponding time-period, the increase in ΔH_R for heat-moisture treated starches were: 2.6 (wheat), 1.6 (oat), and 3.8 (lentil). Whereas in potato starch, ΔH_R decreased by 1.5 J/g (Table 3).

Since in all four starches, $T_c - T_0$ for retrogradation (Table 3) is broader than that for gelatinization (Table 2), it implies that the retrogradation endotherm probably reflects melting of crystallites of different size, stability, or perfection formed by different types of starch chain associations (amylose–amylopectin and/or amylopectin–amylopectin) during gel storage. It is likely, that the bonding forces within crystallites of retrograded starches are weaker (due to improper alignment of the starch chains during reassociation) than those in crystallites of native granules. This is based on the observation, that T_0 , T_p , and T_c of retrograded starches (Table 3) are lower than those for gelatinized starches (Table 2). The gradual increase in ΔH_R is more pronounced in wheat and oat starches (Table 3), due to their higher lipid content (Table 1).

It has been shown [31], that during heat–moisture treatment, crystallinity is enhanced within granules of wheat, oat, and lentil starches (wheat > lentil > oat), but is disrupted in potato starch. Thus, after heat–moisture treatment, the degree of separation between the outer branches of adjacent amylopectin chain clusters would be decreased in wheat, oat and lentil starches, but increased in potato starch. Consequently, during gel storage, the formation and lateral association of double helices involving amylopectin chains, would be easier and much stronger in heat–moisture treated potato starch. This would then explain the observed increase (wheat, oat, and lentil) and decrease (potato) in ΔH_R during retrogradation of heat–moisture treated starches (Table 3). If changes in crystallinity on heat–moisture treatment was the sole factor influencing ΔH_R , then the extent of increase in ΔH_R should have followed the trend: wheat > lentil > oat. However, as seen in Table 3, the foregoing order was reversed with respect to wheat and lentil (lentil > wheat) starches. This suggests, that interaction between amylose and amylopectin chains during gel storage may have also influenced changes in ΔH_R . The amylose and amylopectin chains of lentil [52] starch have been shown to be longer than those of wheat starch [51]. Furthermore, as shown in Table 4, the decrease in amylose leaching on heat–moisture treatment is higher in lentil than in wheat starch. Therefore, the probability of interaction between amylose and amylopectin chains (within gelatinized granules) during storage would be greater in lentil starch. Similar interactions between amylose and amylopectin chains may have also contributed to changes in ΔH_R in heat–moisture treated potato starch [since the chain length of the starch components and the decrease in amylose leaching (Table 4) is much higher than in the other starches]. However, the extent of the foregoing contribution cannot be properly assessed, since crystallite disruption in potato starch on heat–moisture treatment is so extensive [31], that is probably negates any influence that amylose–amylopectin interaction may have had on ΔH_R .

Gel strength (after a storage period of 1 day at 25°C) of all treated starches were higher than those of their native counterparts (Table 5). Defatting increased the gel strength to a greater extent than heat–moisture treatment in wheat and oat starches. Whereas in potato and lentil starches the increase in gel firmness was more pronounced after heat–moisture treatment than on defatting (Table 5). As seen in Table 4, the swelling factor (SF) of all starches decreased on defatting, and

Table 4

Swelling factor, and amylose leaching of native, and treated starches at 95°C

Starch source and treatment	Swelling factor ^{a,b} at 95°C	Amylose leaching ^{a,c} at 95°C
Wheat		
Native	27.6	10.9
Defatted	24.0	11.6
Heat-moisture treated	17.2	7.4
Oat		
Native	25.7	12.3
Defatted	22.7	13.8
Heat-moisture treated	16.1	7.7
Lentil		
Native	93.1	18.3
Defatted	14.1	22.6
Heat-moisture treated	11.2	18.6
Potato		
Native	93.1	18.3
Defatted	29.9	10.8
Heat-moisture treated	13.4	7.1

^a Values are means of 3 determinations.^b Standard deviation, 0.4.^c Standard deviation, 0.3%.

Table 5

Gel strength of native, and treated gels after storage at 25°C

Starch source and treatment	Gel strength ^a (g)
Wheat	
Native	25
Defatted	42
Heat-moisture treated	30
Oat	
Native	11
Defatted	22
Heat-moisture treated	13
Lentil	
Native	101
Defatted	182
Heat-moisture treated	230
Potato	
Native	23
Defatted	41
Heat-moisture treated	80

^a Values are average of three determinations; average SD, 0.55 g.

heat–moisture treatment. Amylose leaching increased in defatted wheat and oat starches, but decreased in defatted potato and lentil starches. However, in all starches, amylose leaching decreased on heat–moisture treatment. Since the short term development of the structure and crystallinity in starch gels is dominated by irreversible ($T < 100^{\circ}\text{C}$) gelation and crystallization of amylose within the gel matrix, an increase in amylose leaching or a decrease in SF (highly swollen granules occurring between adjacent amylose chains would hinder their association during retrogradation) would theoretically be expected to increase gel firmness. In wheat and oat starches, the increase in gel firmness is more pronounced on defatting, since the decreased SF and increased amylose leaching would favor aggregation between amylose chains during gel storage. However, in heat–moisture treated starches, the aggregation between amylose chains during gel storage would be favored only by the decrease in SF, since the decrease in amylose leaching would tend to reduce the amount of amylose chains within the continuous amylose gel matrix. In all four starches, the increase in gel firmness on heat–moisture treatment, suggests that the large decrease in SF (potato > lentil > wheat > oat) negates the influence of decreased amylose leaching on gel firmness.

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