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Impact of annealing and heat-moisture treatment on rapidly digestible, slowly digestible and resistant starch levels in native and gelatinized corn, pea and lentil starches ☆

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ABSTRACT

Impact of annealing (ANN) and heat-moisture treatment (HMT) on rapidly digestible starch (RDS), slowly digestible starch (SDS), resistant starch (RS), and expected glycemic index (eGI) of corn, pea, and lentil starches in their native and gelatinized states were determined. ANN was done for 24 h at 70% moisture at temperatures 10 and 15 °C below the onset (T_o) temperature of gelatinization, while HMT was done at 30% moisture at 100 and 120 °C for 2 h. The swelling factor (SF), amylose leaching (AML) and gelatinization parameters of the above starches before and after ANN and HMT were determined. SF and AML decreased on ANN and HMT (HMT > ANN). The gelatinization temperatures increased on ANN and HMT (HMT > ANN). However, the gelatinization temperature range decreased on ANN but increased on HMT. Birefringence remained unchanged on ANN but decreased on HMT. The Fourier transform infrared (FT-IR) absorbance ratio of 1047 cm^{-1}/1022 cm^{-1} increased on ANN but decreased on HMT. ANN and HMT increased RDS, RS and eGI levels and decreased SDS levels in granular starches. HMT had a greater impact than ANN on RDS, RS, and SDS levels. In gelatinized starches, ANN and HMT decreased RDS and eGI, but increased SDS and RS levels. These changes were more pronounced on HMT. This study showed that amylopectin structure and interactions formed during ANN and HMT had a significant impact on RDS, SDS, RS and eGI levels of starches.

1. Introduction

Starch is classified into rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) according to the rate of glucose release and its absorption in the gastrointestinal tract (Englyst, Kingman, & Cummings, 1992). RDS is the starch fraction that causes a sudden increase in blood glucose level after ingestion, and SDS is a starch fraction that is digested completely in the small intestine at a lower rate as compared to RDS. RS is the starch portion that cannot be digested in the small intestine, but is fermented in the large intestine. A number of physiological effects have been ascribed to RS (Haralampu, 2000; Sajilata, Singhal, & Kulkarni, 2006), whereas studies on the health benefits of SDS are limited (Lehmann & Robin, 2007). The health benefits of RS have been reported as prevention of colon cancer, hypoglycemic effects, substrate for growth of the probiotic microorganisms, reduction of gall stone formation, hypocholesterolemic effects, inhibition of fat accumulation, and increased absorption of minerals (Sajilata et al., 2006). The potential health benefits of SDS are linked to a stable glucose metabolism, diabetes management, mental performance, and satiety (Lehmann & Robin, 2007). Among granular starches, maize, waxy maize, sorghum and legume starches have been shown to contain high amounts of SDS, due to the interplay of optimal granule size, channelisation and the interaction of protein or other surrounding material (Lehmann & Robin, 2007; Zhang, Ao, & Hamaker, 2006; Zhang, Venkatachalam, & Hamaker, 2006).

The glycemic index (GI), which characterizes the carbohydrate in different foods, is ranked on the basis of the postprandial increase in blood glucose (Jenkins, 2007; Jenkins et al., 1982). Low GI foods, by virtue of the slow digestion and absorption of their carbohydrate, produce a more gradual rise in blood glucose and insulin levels, and are increasingly associated with health benefits. Low GI foods have thus been associated with reduced incidence and prevalence of heart disease, diabetes, and also some forms of cancer (Brand-Miller, 2007; Brand-Miller, Hayne, Petocz, & Colagiuri, 2003; Jenkins, 2007; Roberts, 2000; Wolever & Mehling, 2002). FAO/WHO (1998) recommended an increased intake of low GI foods, with emphasis on diabetics and subjects with

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impaired glucose tolerance. In the recent WHO reports (FAO/WHO, 2003), the preventive potential of low GI diets in relation to obesity and diabetes was graded as 'possible'. The evidence for such a possibility was recently strengthened by many clinical studies demonstrating a positive relation between dietary GI and insulin resistance, and prevalence of metabolic syndrome (Brand-Miller, 2007; Jenkins, 2007; Mckeown et al., 2004). In accordance with the definition, the GI must be confirmed *in vivo* by clinical trials. However, GI evaluation in human can be difficult and costly, therefore studies measuring *in vitro* digestion have been done in order to expect *in vivo* effects (Goni, Garcia-Alonso, & Saura-Calixto, 1997; Granfeldt, Björck, Drews, & Tovar, 1992). They suggested that the *in vitro* procedure had a high correlation with *in vivo* glycemic response and thus could be useful in the estimation of the GI. Legume starches have been known to exhibit a lower glycemic index than cereal or tuber starches due to high levels of amylose, large amount of viscous soluble dietary fiber and strong interactions between amylose chains (Hoover & Zhou, 2003).

Annealing (ANN) and heat-moisture treatment (HMT) are two hydrothermal methods that have been used to modify starch digestibility. ANN of starch is a physical treatment of starch granules in the presence of heat and water. During ANN starch granules in excess (>60% w/w) or at intermediate water content (40% w/w) are held at a temperature above the glass transition temperature (T_g) but below the onset (T_o) temperature of gelatinization for a set period of time (Hoover & Vasanthan, 1994a; Tester & Debon, 2000). The following changes have been shown to occur in all starches on ANN: (1) increase in granule stability, (2) crystalline perfection, (3) starch chain interactions within the amorphous and crystalline domains of the granule, (4) formation of double helices, (5) increase in gelatinization temperatures, (6) narrowing of the gelatinization temperature range, (7) decrease in granular swelling, and (8) decrease in amylose leaching. However, depending on the starch source, crystallinity, amylose–lipid interactions, and susceptibility towards acid and enzyme hydrolysis have been shown to increase, decrease or remain unchanged on ANN (Hoover & Manuel, 1996a; Hoover & Vasanthan, 1994a; Jacobs & Delcour, 1998; Tester & Debon, 2000; Waduge, Hoover, Vasanthan, Gao, & Li, 2006). HMT is also a physical modification technique that involves treatment of starch granules at low moisture levels (<35% moisture w/w) for a certain time period (15 min–16 h) and at temperatures (84–120 °C) above T_g but below the gelatinization temperature. In all starches, increase in gelatinization temperatures, widening of the gelatinization temperature range, decrease in granular swelling and amylose leaching, and an increase in thermal stability have been shown to occur on HMT. However, depending on the starch source, changes to the X-ray pattern (B to A + B), formation of amylose–lipid complexes, disruption of crystallinity, and increase or decrease in enzyme susceptibility have also been shown to occur on HMT (Gunaratne & Hoover, 2002; Hoover & Manuel, 1996b; Hoover & Vasanthan, 1994b).

Several attempts have been made to generate RS by ANN and HMT (Brumovsky & Thompson, 2001; Haralampu, 2000; Haralampu & Gross, 1998; Jacobasch, Dongowski, Schmiedl, & Muller-Schmehl, 2006; Lehmann & Robin, 2007; Sajilata et al., 2006; Shi & Trzasko, 1997; Vasanthan & Bhatty, 1998). However, there is a dearth of information on the effect of ANN and HMT on the formation of SDS. Shin, Kim, Ha, Lee, and Moon (2005) showed that the hydrothermal treatment (50% moisture at 55 °C for 12 h) of sweet potato starch increased the SDS level from 15.6% to 31.0%. Niba (2003) investigated the effect of heat treatment, storage temperature and time on the digestibility of various flours (maize, yam, rice, potato, plantain, and cocoyam). For all flours, the SDS content was increased by autoclaving and parboiling, but significantly reduced by microwaving, compared with the raw flour. However, the increased RS and SDS in granular starch by ANN and HMT were not heat stable. The lack of thermal stability of SDS and RS represents a limitation on their use as food ingredients.

The objective of this study was to compare the impact of ANN and HMT (under different time–temperature regimes) on SDS, RS and eGI levels in different starch sources (corn, pea and lentil starches) subjected to *in vitro* α-amylolysis.

2. Materials and methods

2.1. Materials

Pea (*Pisum sativum* L.) cultivar (*1674-13*) and lentil (*Lens culinaris*) cultivar *(CDC Meteor*) were obtained from the Crop Development Centre, University of Saskatchewan, Canada. Pea and lentil starches were extracted from seeds using the procedure of Chung et al. (2008). Normal corn starch (cat. no. S-4126), pancreatin from porcine pancreas (cat. no. P-7545, activity 8× USP/g) and invertase (ED 3.2.1.26) grade VII from Bakers yeast (355 U/mg) were purchased from Sigma Chemical Company (St. Louis, MO, USA). Amyloglucosidase (EC 3.2.1.3., 3300 U/mL) and glucose oxidase-peroxidase assay kit (cat. no. K-GLUC) were purchased from Megazyme (Megazyme International Ireland Ltd., Bray, Ireland).

2.2. Hydrothermal treatment

2.2.1. Annealing

Starch slurries (70% moisture) were incubated at 10 and 15 °C below the onset temperature (T_o) of gelatinization for 24 h in a water bath. At the end of the incubation period, samples were centrifuged (2000*g*) for 10 min and supernatant was decanted (no amylose or soluble carbohydrate was detected in the supernatant). The annealed starches were washed once with deionized water and air dried at room temperature, ground and passed through a 120-mesh screen.

2.2.2. Heat-moisture treatment

Starch samples 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 at 100 or 120 °C for 2 h. Afterwards the containers were opened, and the starch samples air dried to uniform moisture content (∼10%).

2.3. Apparent amylose content

Apparent amylose content was determined using the method of Williams, Kuzina, and Hlynka (1970).

2.4. Amylopectin chain length distribution

Isoamylase debranching of whole starch accompanied by high performance anion exchange chromatography with pulsed amperometric detection (HPAEC–PAD) was used to determine the average chain length (CL) and the branch chain length distribution of the native starches (Liu, Gu, Donner, Tetlow, & Emes, 2007).

2.5. Swelling factor (SF)

SF of native, ANN, and HMT starches when heated at 80 °C in excess water was measured according to the method of Tester and Morrison (1990). The SF is reported as the ratio of the volume of swollen granules to the volume of dry starch.

2.6. Amylose leaching (AML)

Starches (20 mg) in water (10 ml) were heated at 80 °C in sealed tubes for 30 min. The tubes were then cooled to room temperature and centrifuged at 2000g for 10 min. The supernatant (1.0 ml) was withdrawn and its amylose content was determined as described by Williams et al. (1970). AML was expressed as percentage of amylose leached per 100 g of dry starch.

2.7. Differential scanning calorimetry (DSC)

The gelatinization transition temperatures and the enthalpy of gelatinization of native, ANN, and HMT starches were determined using a differential scanning calorimeter (2920 Modulated DSC, TA Instruments, New Castle, DE, USA) equipped with a refrigerated cooling system. The starch (12 mg) and distilled water (28 μl) was added to a high-volume pan and immediately sealed. The sealed pans were reweighed and allowed to stand overnight at room temperature before DSC analyses. The sample pans were heated from 5 to 180 °C at a heating rate of 10 °C/min. An empty pan was used as a reference.

2.8. Polarization light microscopy

Birefringence of native, ANN, and HMT starch granules were observed under polarized light with a binocular microscope (DME, Leica Canada, Mississauga, ON, Canada) equipped with real time viewing (Micropublisher 5.0, QImaging, Surrey, BC, Canada). The images were recorded at the same magnification (400×) for all starch samples (1.0% starch suspension).

2.9. Fourier transform infrared spectroscopy (FT-IR)

Infrared spectra of native, ANN, and HMT starches were recorded on a Digilab FTS 7000 spectrometer (Digilab USA, Randolph, MA) equipped with a thermoelectrically cooled deuterated tri-glycine sulfate (DTGS) detector using an attenuated total reflectance (ATR) accessory at a resolution of 4 cm^{-1} by 128 scans. Spectra were baseline-corrected, and then deconvoluted by drawing a straight line between 1200 and 800 cm^{-1} (using Win-IR Pro software). A half-band width of 15 cm^{-1} and a resolution enhancement factor of 1.5 with Bessel apodization were employed. Intensity measurements were performed on the deconvoluted spectra by recording the height of the absorbance bands from the baseline.

2.10. In vitro starch digestibility

2.10.1. Granular native starch

In vitro starch digestibility was determined following the method described by Englyst et al. (1992) with modifications. Porcine pancreatic α-amylase (0.45 g) was dispersed in water (4 ml), and centrifuged at 1500g for 12 min. The supernatant (2.7 ml) was transferred to a beaker, and amyloglucosidase (0.3 ml) and invertase (0.2 ml) were added to the solution. This enzyme solution was freshly prepared for each digestion. Starch (100 mg) and 4 ml of 0.5 M sodium acetate buffer (pH 5.2) were added to each test tube. The enzyme solution (1 ml) and 15 glass beads (4 mm diameter) were added to each tube which was incubated in a shaking water bath (37 °C, 200 strokes/min). Aliquots (0.1 ml) were taken at intervals and mixed with 1 ml of 80% ethanol. The hydrolyzed glucose content was measured by the glucose oxidase-peroxidase reagent.

Starch classifications based on the rate of hydrolysis were: rapidly digestible (digested within 20 min) starch (RDS), slowly digestible (digested between 20 and 180 min) starch (SDS) and resistant (undigested after 180 min) starch (RS).

2.10.2. Gelatinized starch

The native, ANN, and HMT starches (100 mg) and water (2 ml) were added to test tubes. The tubes were capped, and the contents were mixed by vortexing for 1 min. The tubes were heated in boiling-water bath for 20 min while gently stirring magnetically at low speed. After heating, the tube was placed in a water bath at 37 °C to equilibrate for 10 min. The above procedure of digestibility was followed.

2.11. Expected glycemic index (eGI)

The expected glycemic index (eGI) of native, ANN and HMT starch was calculated in accordance with the procedure established by Granfeldt et al. (1992). The hydrolysis index (HI) was obtained by dividing the area under the hydrolysis curve of the sample by the area obtained for a standard material (white bread). The expected glycemic index (eGI) was calculated using the equation (Granfeldt et al., 1992) shown below:

$$eGI = 8.198 + 0.862\ HI.$$

3. Results and discussion

3.1. Amylose content and amylopectin structure

The apparent amylose content and the amylopectin chain length distribution of corn, pea, and lentil starches are presented in Table 1. The apparent amylose content of corn, pea, and lentil starches was 24.6%, 35.4%, and 36.9%, respectively. The proportion of short A chains (DP 6–12) of corn starch (31.6%) was higher than that of pea (24.1%) and lentil (26.9%) starches, whereas the proportion of B1 (DP 13–24, 55.3%) and B2 chains (DP 25–36, 13.1%) of corn starch were lower than those of pea (59.9% and 16.0%) and lentil (57.8% and 15.3%) starches. The average chain length (CL) of corn starch was also lower (16.0) than that of pea (17.6) and lentil (17.3) starches.

3.2. Amylose leaching (AML) and swelling factor (SF)

Studies on AML and SF provide information on the extent of interaction between starch chains in the amorphous and crystalline domains of the native granule. The extent of AML and SF of native, ANN, and HMT starches at 80 °C are presented in Fig. 1. The extent of AML in native starches followed the order: lentil > pea > corn. The higher extent of AML in pea and lentil starches could be attributed to their higher amylose content (Table 1) and to the presence of only trace quantities (<0.27%) of amylose complexed lipids (Hoover & Manuel, 1996a; Ratnayake, Hoover, Shahidi, Perera, & Jane, 2001). Amylose complexed lipids in corn starch have been shown to be in the range of 0.68–0.78% (Hoover & Manuel, 1996b; Jayakody & Hoover, 2002). In both pea and lentil

Table 1
Apparent amylose content, average chain length and chain length distribution of corn, pea and lentil starches [a]

Starch source	Apparent amylose content (%)	Average chain length (CL)	Percent distribution (%)		
			DP[b] 6–12 (A chains)	DP[b] 13–24 (B1 chains)	DP [b]25–36 (B2 chains)
Corn	24.6 ± 0.3	16.0 ± 0.1	31.6 ± 1.2	55.3 ± 1.4	13.1 ± 0.1
Pea	35.4 ± 0.3	17.6 ± 0.3	24.1 ± 1.8	59.9 ± 0.9	16.0 ± 0.9
Lentil	36.9 ± 0.2	17.3 ± 0.0	26.9 ± 0.6	57.8 ± 0.5	15.3 ± 0.2

[a] Mean (± standard deviation) of duplicate analysis.
[b] DP, degree of polymerization.

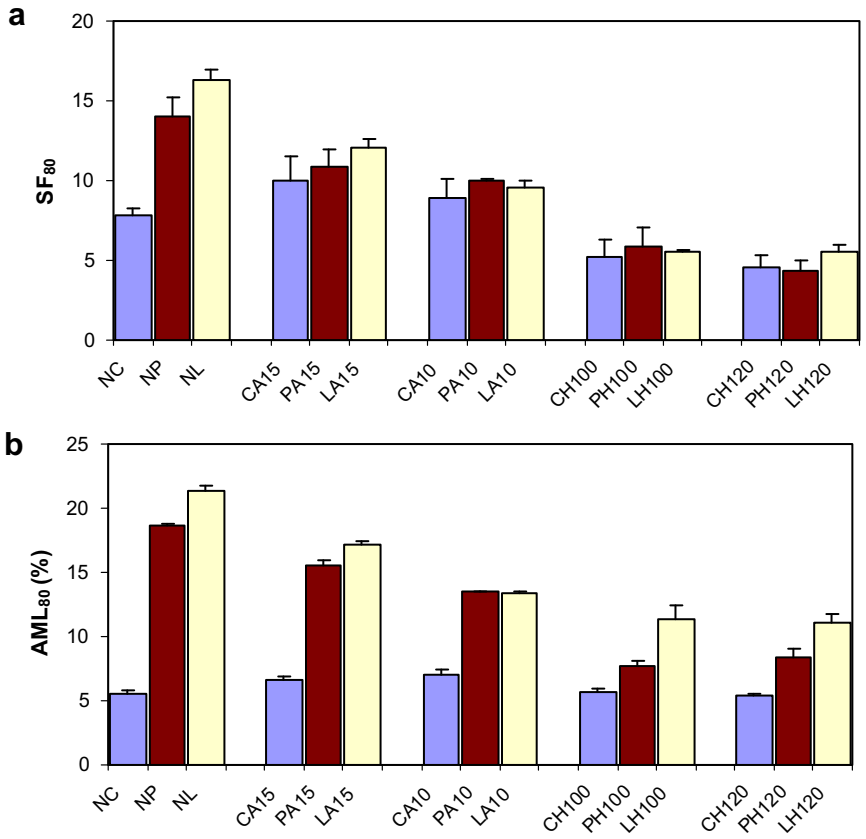

Fig. 1. Swelling factors (a) and amylose leaching (b) of native (N), annealed (A) and heat-moisture treated (H), corn (C), pea (P) and lentil (L) starches at 80 °C. CA10, PA10, LA10 and CA15, PA15, LA15 represent corn, pea and lentil starches annealed for 24 h at 10 and 15 °C below the onset (T_o) temperature of gelatinization, respectively. CH100, PH100, LH100 and CH120, PH120, LH120 represent corn, pea and lentil starches heat-moisture treated at 30% moisture for 2 h at 100 and 120 °C, respectively.

starches, AML decreased on ANN and HMT. The extent of this decrease on HMT was higher than that observed on ANN. AML increased slightly in corn starch on ANN. However, there was no significant difference in AML on HMT (Fig. 1). The decrease in AML on ANN and HMT has been attributed to: (1) additional interaction between AM–AM and/or AM–AMP chains and (2) increase in the amount of lipid complexed amylose chains (Hoover & Vasanthan, 1994a; Hoover & Vasanthan, 1994b; Tester, Debon, & Sommerville, 2000). In this study, the decrease in AML is mainly due to the former, since only trace quantities of lipids are associated with starch granules of pea and lentil starches (Hoover & Manuel, 1996b; Ratnayake et al., 2001). HMT decreases AML to a greater extent than ANN since the thermal energy imparted to amylose chains is higher during HMT, resulting in increased mobility, thereby facilitating interaction. The decrease in AML on ANN and HMT is more pronounced in pea and lentil starches than in corn starch due to their higher proportion of long B1 and B2 amylopectin chains (Table 1) and higher amylose content (Table 1).

Swelling factor (SF) has been shown to be influenced by: (1) amylopectin structure (Sasaki & Matsuki, 1998; Shi & Seib, 1992; Tester, Morrison, & Schulman, 1993) and (2) lipid complexed amylose chains (Tester & Morrison, 1990; Tester et al., 1993). The SF of the native starches followed the order: lentil > pea > corn. The relative crystallinity of pea, lentil (Chung et al., 2008) and corn (Srichuwong, Sunarti, Mishima, Isono, & Hisamatsu, 2005) has been shown to be 25%, 28% and 32%, respectively. This suggests that the differences in SF among the native starches is influenced by differences in their crystallinity and also by the amount of lipid complexed amylose chains (corn > lentil ~ pea). SF of pea and lentil starches decreased (pea ~ lentil) on ANN and HMT. However, the SF of corn starch increased on ANN, but decreased on HMT (Fig. 1). The extent of these changes was more pronounced on HMT. The decrease in SF could be attributed to increased crystallite perfection and to additional interaction between AM–AM and/or AM–AMP chains (Hoover & Vasanthan, 1994a). The extent of the decrease in SF is lower in corn than in pea and lentil starches due to its lower amylose content and lower proportion of long amylopectin chains (Table 1).

3.3. Gelatinization characteristics

The gelatinization transition temperatures (onset [T_o], peak [T_p], and conclusion [T_c]), gelatinization transition temperature range (T_c–T_o), and gelatinization enthalpy (ΔH) of native, ANN, and HMT starches are presented in Table 2 and Fig. 2. T_o, T_p and T_c have been shown to be influenced by amylose content (Demeke, Hucl, Abdel-Aal, Baga, & Chibbar, 1999; Inouchi et al., 1993; Stevenson, Doorenbus, Jane, & Inglett, 2006), amylopectin chain length distribution (Stevenson et al., 2006; Vandeputte, Vermeylen, Geeroms, & Delcour, 2003) and lipid complexed amylose chains (Hoover & Ratnayake, 2002; Vandeputte et al., 2003). Cooke and Gidley (1992) have shown that ΔH reflects the loss of double helical order. The higher T_o, T_p and T_c for corn starch reflect its higher amylopectin content (Table 1), whereas its lower ΔH reflects the higher proportion of A chains with a DP of 6–12. These chains are too short to form stable double helices, and thus less energy would be required to unravel and melt these double helices during gelatinization. The higher T_c–T_o for pea and lentil starches reflects greater variation in crystalline stability. ANN at T_o–10 °C and T_o–15 °C increased T_o, T_p and T_c, and decreased T_c–T_o in all starches. The extent of these

Table 2
Gelatinization characteristics of native, annealed, and heat-moisture treated starches[a]

Sample	T_o (°C)[b]	T_p (°C)[b]	T_c (°C)[b]	$T_c - T_o$ (°C)	ΔH (J/g)[c]
NC[d]	67.3 ± 0.6	72.9 ± 0.7	82.7 ± 1.6	15.5 ± 1.0	10.9 ± 0.5
NP[d]	59.1 ± 0.1	66.3 ± 0.1	80.1 ± 0.4	21.0 ± 0.4	14.1 ± 0.1
NL[d]	63.1 ± 0.2	69.9 ± 1.0	83.4 ± 1.5	20.3 ± 1.7	13.5 ± 0.3
CA15[e]	72.5 ± 0.4	76.5 ± 0.8	85.0 ± 0.8	12.5 ± 0.4	11.5 ± 0.6
PA15[e]	67.5 ± 0.4	71.5 ± 0.1	84.2 ± 0.3	16.7 ± 0.1	14.0 ± 0.4
LA15[e]	71.8 ± 0.0	75.0 ± 0.1	86.8 ± 0.4	15.0 ± 0.0	13.5 ± 0.4
CA10[f]	74.4 ± 0.2	77.6 ± 0.3	86.1 ± 0.2	11.7 ± 0.0	10.2 ± 0.3
PA10[f]	71.2 ± 0.2	74.6 ± 0.4	87.3 ± 0.5	16.2 ± 0.3	12.4 ± 0.3
LA10[f]	75.0 ± 0.9	78.4 ± 0.9	90.0 ± 0.9	15.0 ± 0.0	12.0 ± 0.7
CH100[g]	71.9 ± 0.8	82.1 ± 0.4	90.6 ± 0.1	18.7 ± 0.9	7.5 ± 0.5
PH100[g]	69.4 ± 0.5	83.4 ± 0.6	94.2 ± 1.0	24.8 ± 0.5	7.9 ± 0.1
LH100[g]	72.5 ± 1.0	84.7 ± 1.4	94.5 ± 1.1	22.0 ± 0.1	9.6 ± 0.3
CH120[h]	67.8 ± 0.4	82.2 ± 0.6	88.8 ± 0.7	21.0 ± 0.3	6.1 ± 0.3
PH120[h]	64.3 ± 0.2	88.6 ± 0.2	97.5 ± 0.9	33.2 ± 1.0	7.1 ± 0.1
LH120[h]	65.9 ± 0.2	86.4 ± 0.1	96.3 ± 0.8	30.4 ± 0.6	8.0 ± 0.0

[a] Mean (±standard deviation) of duplicate analysis.
[b] T_o, T_p, and T_c indicate the temperatures of the onset, peak, and conclusion of gelatinization, respectively.
[c] Enthalpy of gelatinization.
[d] NC, NP, NL – unmodified corn, pea and lentil starches.
[e] Annealed (T_o−15 °C, 70% moisture, 24 h) corn (CA15), pea (PA15) and lentil (LA15) starches.
[f] Annealed (T_o−10 °C, 70% moisture, 24 h) corn (PA10), pea (PA10) and lentil (LA10) starches.
[g] Heat-moisture treated (100 °C, 30% moisture, 2 h) corn (CH100), pea (PH100) and lentil (LH100) starches.
[h] Heat-moisture treated (120 °C, 30% moisture, 2 h) corn (CH120), pea (PH120) and lentil (LH120) starches.

changes was more pronounced at T_o−10 °C (Table 2). These changes have been attributed to perfection of pre-existing crystallites (Hoover & Vasanthan, 1994a; Jacobs & Delcour, 1998; Waduge et al., 2006). The extent of increase in T_o, T_p and T_c ($T_o > T_p > T_c$) at T_o−10 °C and T_o−15 °C, followed the order: lentil > pea > corn. ANN has a greater influence on T_o, since T_o represents melting of the weakest crystallites (Larsson & Eliasson, 1991; Nakazawa & Wang, 2003). These crystallites are more susceptible to crystallite perfection on ANN than crystallites that have a higher stability (represented by T_c) (Jacobs, Eerlingen, Spaepen, Grobet, & Delcour, 1998). Hoover and Vasanthan (1994a) have postulated that the main type of interaction influencing increases in T_o, T_p and T_c on ANN is that between amylose and the outer branches of amylopectin. The greater increases in T_o, T_p and T_c for pea and lentil starches, on ANN, suggests that interaction between amylose and the outer branches of amylopectin are more pronounced than in corn starch. This could be attributed to their higher amylose content (Table 1), longer average chain length (CL) of amylopectin (Table 1), lower proportion of short A chains of DP 6–12 (Table 1) and their longer amylose chains. The chain length of amylose has been reported to be DP 1400 for lentil (Biliaderis, Grant, & Vose, 1981), DP 1300 for pea (Ratnayake et al., 2001) and DP 990 for corn (Takeda, Shitaozono, & Hizukuri, 1988). The order of the extent of decrease in $T_c - T_o$ (lentil ∼ pea > corn) (Table 2) on ANN, could be attributed to crystallites of corn starch not being properly aligned in the native granule due to a higher proportion of short A chains of DP 6–12.

HMT at 100 and 120 °C increased T_o, T_p, T_c ($T_p > T_c > T_o$) and $T_c - T_o$ (Table 2 and Fig. 2). The extent of this increase was more pronounced at 120 °C, and followed the order: pea > lentil > corn. Similar changes to T_o, T_p, T_c and $T_c - T_o$ have been reported for cereal (Hoover & Manuel, 1996b; Hoover & Vasanthan 1994b) and legume (Hoover & Manuel, 1996b) starches. Donovan (1979) reported that crystalline and double helical melting during gelatinization are assisted by hydration and swelling of the starch granule amorphous regions. The swelling of the amorphous regions imparts a stress on the crystalline regions, and thereby strips polymer chains from the crystallites. Interaction between AM–AM and/or AM–AMP chains on HMT would suppress the mobility of the amorphous regions. Consequently, the amorphous regions of HMT starch would require a higher temperature to incur swelling that could contribute to the disruption of the crystalline regions. The same factors influencing T_o, T_p and T_c on ANN are also responsible for increase in T_o, T_p and T_c on HMT, being higher in pea and lentil starches than in corn starch.

ANN at T_o−10 °C decreased ΔH of pea and lentil (pea ∼ lentil) starches, but had no influence on ΔH of corn starch (Table 2). However, at T_o−15 °C, the ΔH of all three starches remained unchanged. It is difficult to compare the ΔH with those of published data (Hoover & Manuel, 1996a; Tester et al., 2000) due to differences in ANN conditions. The decrease in ΔH in pea and lentil starches at T_o−10 °C suggests that double helices formed due to interaction between amylose and the outer branches of amylopectin during biosynthesis of pea and lentil starches (this interaction is highly probable due to their long AM and AMP chains) may have been loosely associated, and hence prone to disruption, when the temperature of ANN (T_o−10 °C) is closer to T_o. The decrease in ΔH on ANN at T_o−10 °C cannot be attributed to gelatinization, since the birefringence pattern (Fig. 3h) and granule morphology (figures not shown) remained unchanged after ANN in both pea and lentil starches. The ΔH of all three starches decreased on HMT. At both temperatures (100 and 120 °C), the extent of the decrease followed the order: pea > lentil > corn (Table 2). Decreased ΔH following HMT has also been reported in jackbean (Lawal & Adebowale, 2005) and corn (Pukkahuta, Suwannawat, Shobsngob, & Varavinit, 2008) starches. However, Hoover and Manuel (1996b) reported no decrease in ΔH on HMT of corn starch at 100 °C. Gunaratne and Hoover (2002) have postulated that the decrease in ΔH on HMT reflects disruption of double helices present in the crystalline and non-crystalline regions of the granule. The greater decrease in ΔH in pea and lentil starches may have been due to weakly associated double helices and to the presence of B-type unit cells. The pea and lentil starches (C-type starch granules) contain both A- and B-types of polymorph. The packing of helices in B-type unit cells is less compact than that in A-type starches. Consequently, on HMT, the double helical chains forming the crystallites of B-type starches would be more mobile and hence more prone to disruption than those of A-type starches. This would then explain the larger decrease of ΔH in pea and lentil starches (Table 2).

3.4. Birefringence

Native corn (Fig. 3a) and pea (Fig. 3f) starches exhibited the characteristic birefringence pattern (maltese cross) under polarized light. Birefringence indicates that the average orientation of the polymer chains is radial. The intensity of birefringence is influenced by granule shape and on the orientation of the granules with respect to the light beam (Buléon, Colonna, Planchot, & Ball, 1998). The intensity of birefringence of corn (Figs. 3b and c) and pea (Figs. 3g and h) starches remained unchanged on ANN. However, HMT decreased birefringence (more pronounced at the granule center) in both corn (Figs. 3d and e) and pea (Figs. 3i and j) starches. The extent of this decrease was higher at 120 °C (Figs. 3e and j). The granule center appeared hollow in both corn (Figs. 3d and e) and pea (Figs. 3i and j) starches. The decreased birefringence intensity at the granule center suggests that the thermal energy imparted to the double helices (forming the crystallites) during HMT may have increased their mobility, thereby resulting in a loss of radial orientation. In both corn (Figs. 3d and e) and pea (Figs. 3i and j) starches, birefringence intensity at the granule periphery remained unchanged on HMT. This suggests that starch chains at the granule center are less organized than those at the periphery, and are therefore more susceptible to reorientation during HMT. Lentil

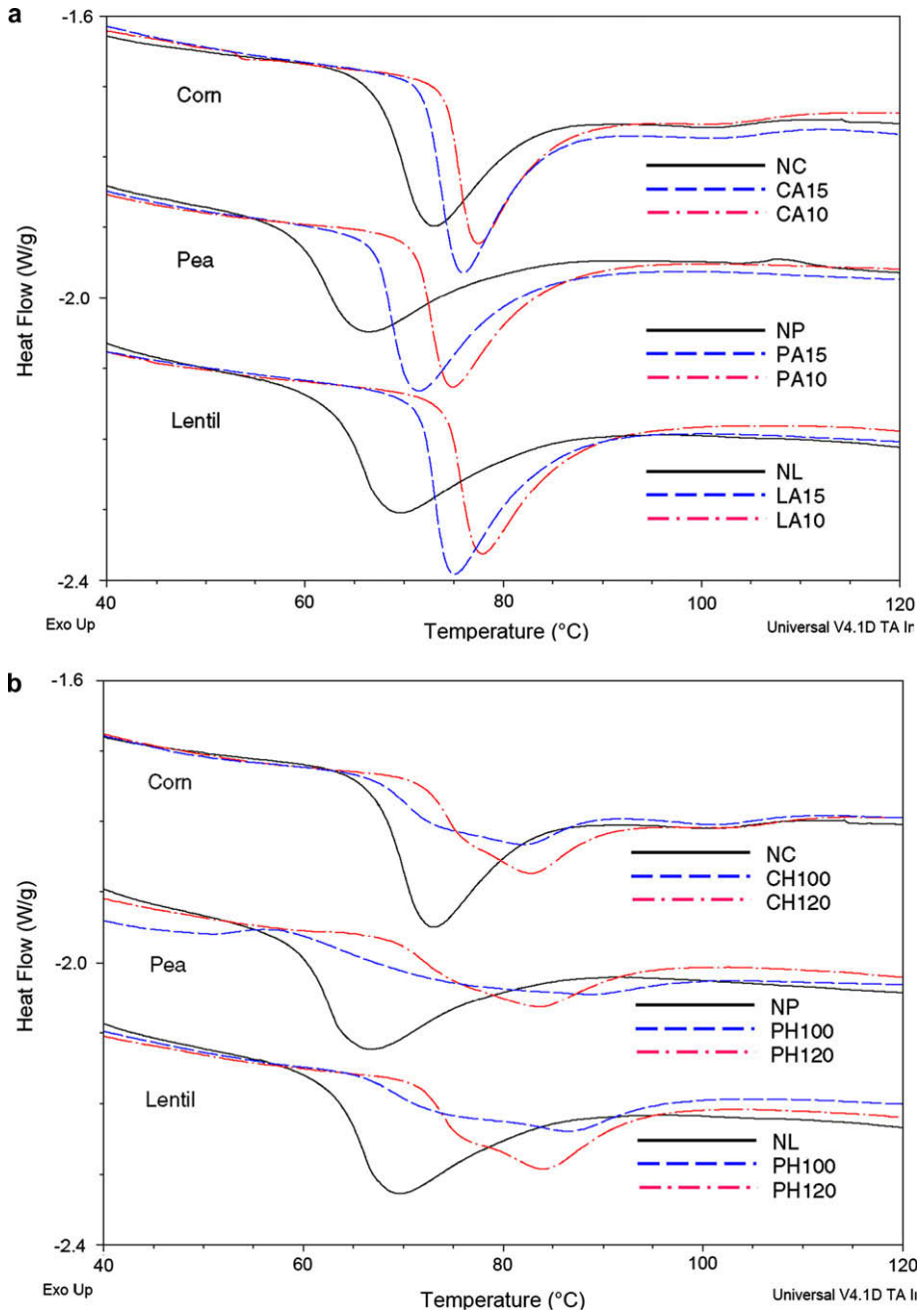

Fig. 2. DSC thermograms of native (N) and annealed (A) corn (C), pea (P) and lentil (L) starches (a), and DSC thermograms of native and heat-moisture treated (H) corn, pea and lentil starches (b). CA10, PA10, LA10 and CA15, PA15, LA15 represent corn, pea and lentil starches annealed for 24 h at 10 and 15 °C below the onset (T_o) temperature of gelatinization, respectively. CH100, PH100, LH100 and CH120, PH120, LH120 represent corn, pea and lentil starches heat-moisture treated at 30% moisture for 2 h at 100 and 120 °C, respectively.

starch behaved similarly (figure not shown) to pea starch on ANN and HMT. The formation of hollow centers on HMT has also been reported for potato and corn starches (Kawabata et al., 1994; Vermeylen, Goderis, & Delcour, 2006).

3.5. FT-IR spectroscopy

The FT-IR spectrum of starch has been shown to be sensitive to changes in structure on a molecular level (short-range order), such as starch chain conformation, crystallinity, and retrogradation (van Soest, Tournois, de Wit, & Vliegenthart, 1995). The IR absorbance bands at 1047 and 1022 cm^{-1} are sensitive to ordered or crystalline structures and amorphous structures in starch (Fig. 4a), respectively and thus the ratio of 1047 cm^{-1}/1022 cm^{-1} has been used to express the amount of ordered crystalline to amorphous domains in starches (Capron, Robert, Colonna, Brogly, & Planchot, 2007; van Soest et al., 1995). The ratios of 1047 cm^{-1}/1022 cm^{-1} for native, ANN, and HMT starches are presented in Fig. 4b. Among the native starches, the ratio followed the order: lentil > pea > corn. ANN at T_o−10 and T_o−15 °C increased the ratio in all starches (pea > lentil ~ corn). This increase can be attributed to crystalline perfection that occurs during ANN (Table 2). However, the ratio decreased on HMT. The extent of this decrease at 120 °C (lentil > pea > corn) was higher than at 100 °C (lentil > pea ~ corn). X-ray diffraction studies have shown that at 30% moisture content, the X-ray intensities of pea (Hoover &

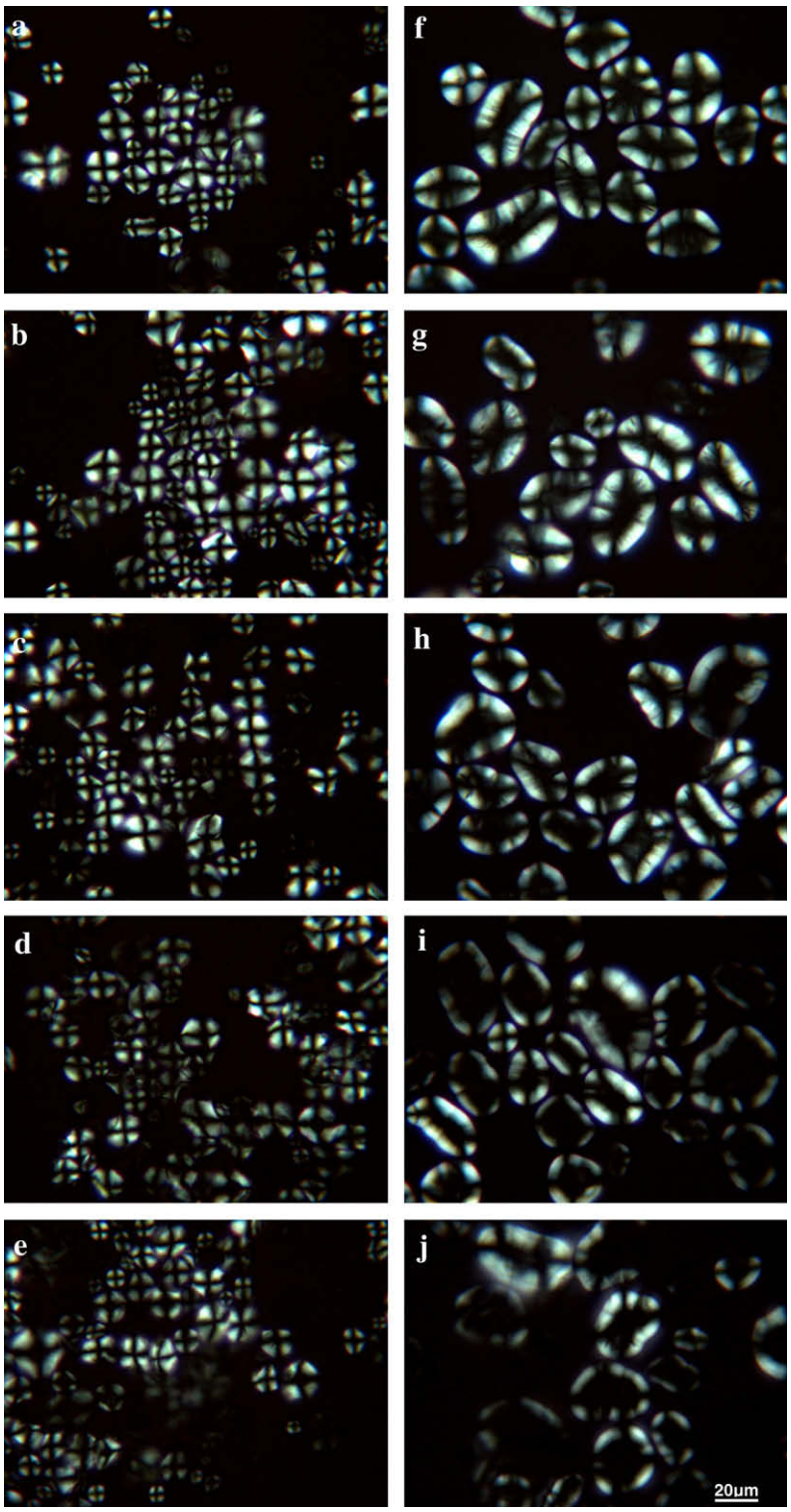

Fig. 3. Photomicrographs of native, annealed and heat-moisture treated corn and pea starches. (a) Native corn starch, (b) corn starch annealed at T_o−15 °C, (c) corn starch annealed at T_o−10 °C, (d) corn starch heat-moisture treated at 100 °C, (e) corn starch heat-moisture treated at 120 °C, (f) native pea starch, (g) pea starch annealed at T_o−15 °C, (h) pea starch annealed at T_o−10 °C, (i) pea starch heat-moisture treated at 100 °C, (j) pea starch heat-moisture treated at 120 °C.

Manuel, 1996a), lentil (Hoover & Manuel, 1996a), and corn (Lim, Chang, & Chung, 2001) decrease slightly on HMT. This decrease may have been due to double helical reorientation within crystalline domains and/or to disruption of few of the hydrogen bonds linking adjacent double helices.

3.6. In vitro digestibility

The enzyme hydrolysis curves of native, ANN and HMT corn, pea and lentil starches, and the amount of rapidly digestible (RDS), slowly digestible (SDS) and resistant (RS) starch are

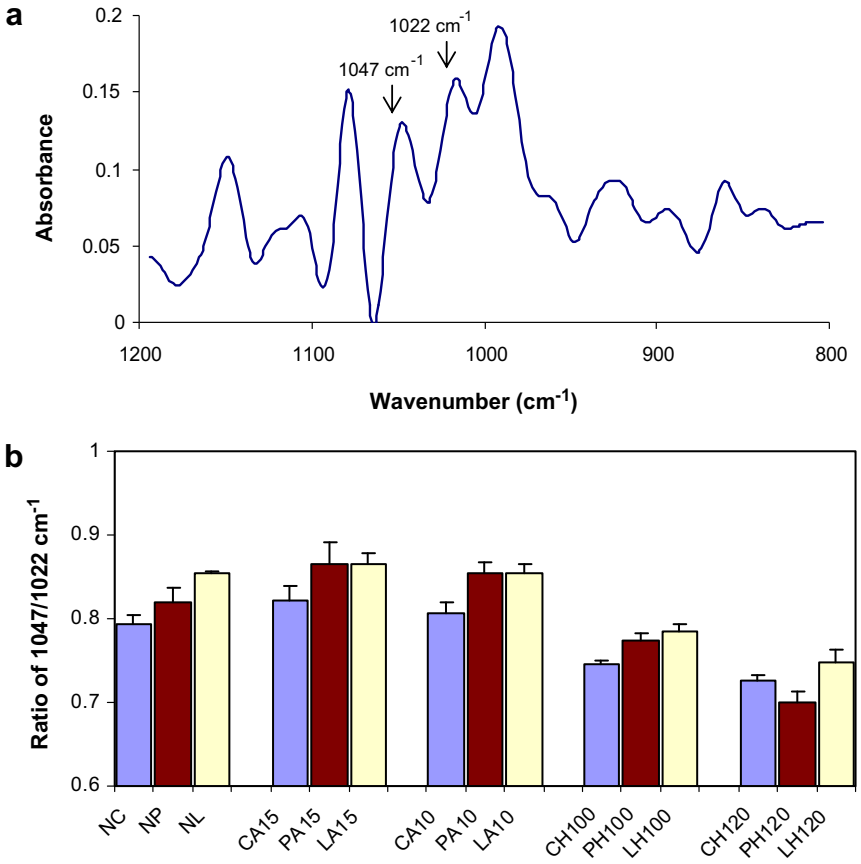

Fig. 4. Deconvoluted Fourier transform infrared spectrum of native pea starch (a), and ratio of the peak heights at 1047 and 1022 cm^{-1} for native, annealed and heat-moisture treated corn, pea and lentil starches (b). CA10, PA10, LA10 and CA15, PA15, LA15 represent corn, pea and lentil starches annealed for 24 h at 10 and 15 °C below the onset (T_o) temperature of gelatinfization, respectively. CH100, PH100, LH100 and CH120, PH120, LH120 represent corn, pea and lentil starches heat-moisture treated at 30% moisture for 2 h at 100 and 120 °C, respectively.

presented in Fig. 5 and Table 3, respectively. The extent of hydrolysis (after 3 h) among the native starches followed the order: corn (95.4%) > lentil (90.9%) > pea (90.0%) (Figs. 5a–c). RDS, SDS and RS levels followed the order: corn > pea > lentil, lentil > corn > pea, and pea > lentil > corn, respectively (Table 3). As shown earlier (Table 2), the proportion of short amylopectin 'A' chains (DP 6–12) is larger in corn than in pea and lentil starches. Double helices formed by 'A' chains are unstable, and are thus easily attacked by hydrolytic enzymes (Gidley & Bulpin, 1987; Zhang, Ao, et al., 2006). Furthermore, 'A' chains disrupt the formation of ordered crystalline structures and negatively affect the perfection of amylopectin crystalline structure (Zhang, Ao, et al., 2006). O'Brien and Wang (2008) have postulated that the presence of branch linkages in the crystalline lamella of 'A'-type (cereal) starches produces 'weak' points that are highly susceptible to hydrolytic enzymes. Whereas, in starches that have a pure B-type (tuber and high amylose starches) or a mixed A + B (legume) crystalline structure, branch points are mostly found in the amorphous region and thereby provide a more superior crystalline structure that is resistant to hydrolysis. This would then explain the difference in enzyme susceptibility among the native starches (Figs. 5a–c). The higher RS levels (Table 3) in pea and lentil starches than corn starch reflects their higher amylose content (Table 1) and longer amylose and amylopectin chain (Table 1) lengths.

ANN at T_o−10 and T_o−15 °C increased (Table 3) RDS and decreased SDS levels in all native granular starches. For instance, the RDS content of lentil starch was 20.8%, 30.4%, and 57.8%, and SDS content was 70.1%, 60.4%, and 30.8% in NL, LA15, and LA10, respectively. ANN increased the RS content of all starches (Table 3). The RS content of native granular starch was 4.6%, 10.0% and 9.1%, and after annealing at T_o−10 °C, the RS content was 8.7%, 11.2%, and 11.4% in corn, pea, and lentil starches, respectively. The extent of these changes are more pronounced at T_o−10 °C (Table 3), since the extent of crystalline perfection is greater than at T_o−15 °C (Table 3). The increase in RDS levels on ANN is probably due to the formation of a more porous structure (O'Brien & Wang, 2008). Formation of a porous structure would allow greater accessibility of hydrolytic enzyme into the granular interior. The increase in RS levels on ANN (Table 3) reflects enhanced interactions between starch chains (AM–AM and/or AM–AMP).

HMT increased RDS and RS and decreased SDS levels in all three native granular starches (Table 3). During the early stages of hydrolysis (0–60 min), HMT starches were hydrolyzed to a greater extent than their native counterparts. However, beyond 180 min, hydrolysis was more pronounced in native starches (Figs. 5a–c). For instance, NC, CH100 and CH120 were hydrolyzed to the extent of 66.3%, 78.5%, and 80.6%, respectively, after 60 min. Whereas, after 180 min, NC, CH100 and CH120 were hydrolyzed to the extent of 95.4%, 89.5%, and 87.7%, respectively. The above changes were more pronounced at 120 °C than at 100 °C (Table 3), due to greater starch chain mobility at 120 °C. The susceptibility to enzyme hydrolysis decreases or increases after HMT depending on starch source, cultivar and treatment conditions. The increased susceptibility toward enzyme hydrolysis following HMT has been observed in pea, bean, lentil (Hoover & Manuel, 1996a), potato, yam and oat starches (Hoover & Vasanthan, 1994b). This was attributed to disrupted

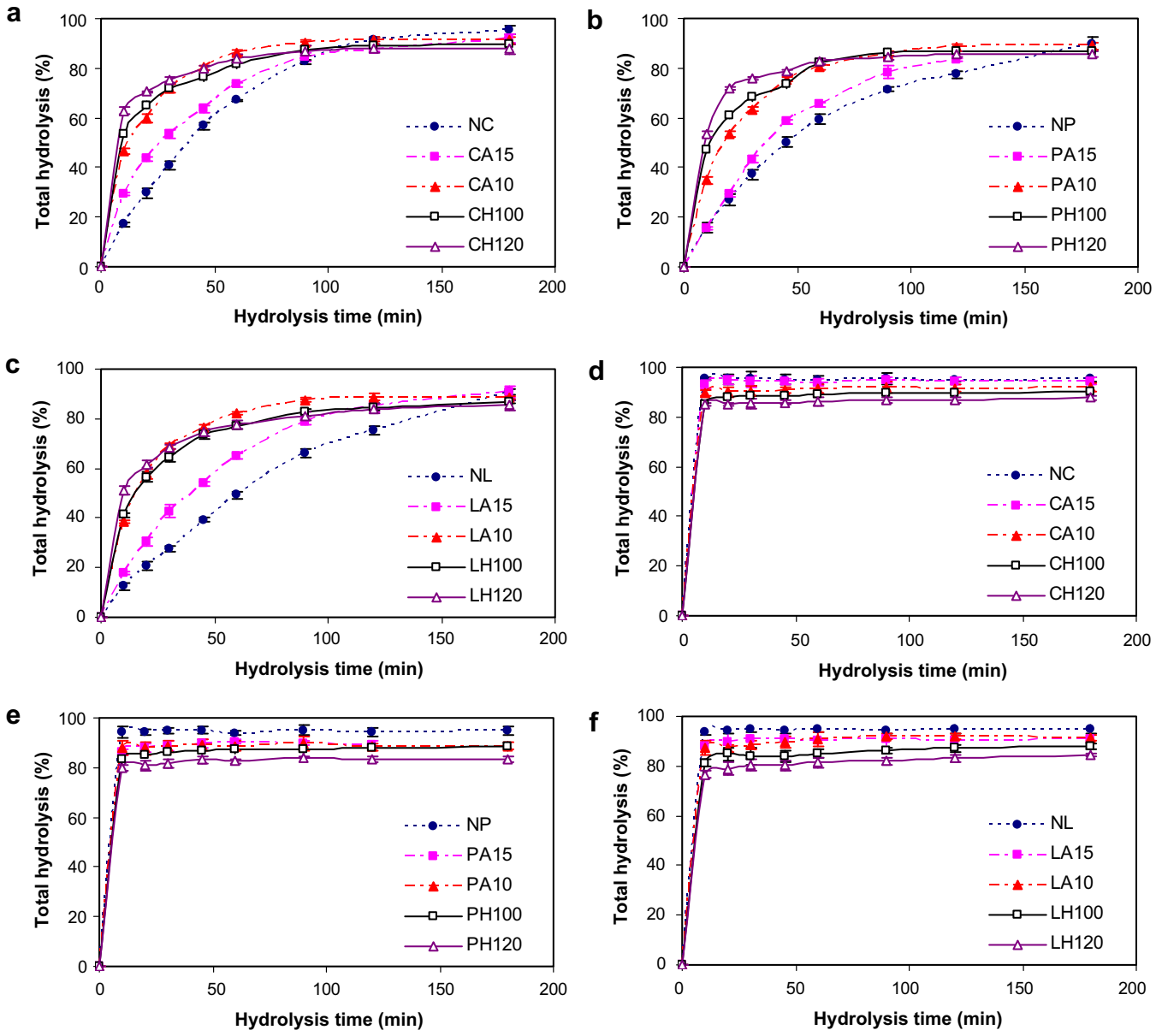

Fig. 5. Enzyme hydrolysis of native, annealed and heat-moisture treated corn, pea and lentil starches in their granular (a–c) and gelatinized (d–f) states. CA10, PA10, LA10 and CA15, PA15, LA15 represent corn, pea and lentil starches annealed for 24 h at 10 and 15 °C below the onset (T_o) temperature of gelatinization, respectively. CH100, PH100, LH100 and CH120, PH120, LH120 represent corn, pea and lentil starches heat-moisture treated at 30% moisture for 2 h at 100 and 120 °C, respectively.

starch crystallites. Decreased enzyme hydrolysis on HMT (due to interaction between starch chains) has been reported for wheat, lentil (Hoover & Vasanthan, 1994b), corn, waxy corn (Franco, Ciacco, & Tavares 1995), and rice starches (Anderson, Guraya, James, & Salvaggio, 2002). The increase in RDS and decrease in SDS on HMT may have been due to disruption of double helices forming the starch crystallites at the granule surface and/or to crystallite reorientation, which was evidenced by a decrease in gelatinization enthalpy (Table 2), loss of birefringence (Fig. 3), and decrease in the amount of ordered crystalline domains to amorphous domains (ratio of 1047 cm^{-1}/1022 cm^{-1}, Fig. 4b). The increase in RS on HMT reflects increased starch chain interaction.

In ungelatinized native, ANN, and HMT starches, the enzyme hydrolyses curve reached a plateau in about 130 min (Figs. 5a–c). However, gelatinization resulted in the plateau being reached in about 10 min (Figs. 5d–f). This is indicative that hydrogen bonds present between starch chains in native starches, and those formed on ANN and HMT, may have been disrupted (thereby increasing the accessibility of the starch chains to hydrolyzing enzymes) during gelatinization. It was interesting to observe, that even after gelatinization, the hydrolysis extent decreased on ANN and HMT (Figs. 5d–f). The RDS content decreased and the RS and SDS contents increased after gelatinization on ANN and HMT (Table 3). Furthermore, changes to RDS, SDS and RS levels on ANN and HMT were more pronounced at T_o−10 °C and at 120 °C, respectively (Table 3). For instance, when the starch was heat-moisture treated at 120 °C, the RDS decreased as compared to gelatinized unmodified starches by 10.2%, 14.0%, and 15.1%, the SDS content increased by 2.5%, 2.8% and 4.7%, and the RS content increased by 7.7%, 11.2% and 10.4% for corn, pea, and lentil starches, respectively. The increase in thermo-stable SDS and RS suggests that some interactions formed during ANN and HMT may have survived after gelatinization, thereby partly restricting accessibility of starch chains to the hydrolyzing enzymes. We believe that the above

Table 3
RDS, SDS and RS levels in native and gelatinized starches subjected to annealing and heat-moisture treatment[a]

Sample	Native starch			Gelatinized starch		
	RDS (%)[b]	SDS (%)[b]	RS (%)[b]	RDS (%)[b]	SDS (%)[b]	RS (%)[b]
NC[c]	29.7 ± 1.9	65.7 ± 1.3	4.6 ± 1.8	95.3 ± 2.0	0.1 ± 0.2	4.6 ± 1.8
NP[c]	27.0 ± 2.5	62.9 ± 0.7	10.0 ± 2.4	94.2 ± 1.0	0.6 ± 1.0	5.2 ± 0.8
NL[c]	20.8 ± 1.8	70.1 ± 2.2	9.1 ± 1.2	93.9 ± 0.6	0.8 ± 0.8	5.3 ± 0.6
CA15[d]	43.4 ± 0.6	48.6 ± 2.2	8.0 ± 1.7	94.7 ± 1.1	0.1 ± 0.2	5.2 ± 1.2
PA15[d]	29.3 ± 1.0	59.8 ± 1.3	10.9 ± 1.3	87.9 ± 1.9	1.9 ± 1.4	10.2 ± 0.6
LA15[d]	30.4 ± 1.6	60.4 ± 1.8	9.2 ± 2.1	90.1 ± 2.5	1.9 ± 0.4	8.0 ± 2.2
CA10[e]	59.9 ± 1.7	31.4 ± 0.3	8.7 ± 1.5	90.2 ± 2.0	1.6 ± 1.1	8.2 ± 1.8
PA10[e]	53.4 ± 1.1	34.4 ± 0.5	11.2 ± 1.3	87.7 ± 2.6	1.8 ± 1.9	10.5 ± 0.8
LA10[e]	57.8 ± 1.7	30.8 ± 1.5	11.4 ± 0.5	89.8 ± 1.5	1.5 ± 1.2	8.7 ± 0.9
CH100[f]	65.2 ± 1.3	24.2 ± 1.4	10.5 ± 1.0	87.9 ± 1.4	2.4 ± 1.3	9.7 ± 0.8
PH100[f]	60.8 ± 0.8	25.9 ± 2.0	13.3 ± 1.5	84.9 ± 1.1	3.5 ± 1.6	11.6 ± 1.7
LH100[f]	56.4 ± 2.0	30.4 ± 2.2	13.2 ± 0.5	81.6 ± 2.4	5.2 ± 2.7	13.2 ± 1.4
CH120[g]	70.4 ± 0.4	17.3 ± 2.2	12.3 ± 1.9	85.1 ± 0.6	2.6 ± 1.3	12.3 ± 0.8
PH120[g]	71.7 ± 0.7	13.8 ± 1.0	14.5 ± 1.2	80.2 ± 1.4	3.4 ± 1.6	16.4 ± 0.4
LH120[g]	61.7 ± 1.6	23.6 ± 3.0	14.7 ± 2.0	78.8 ± 2.5	5.5 ± 2.3	15.7 ± 0.6

[a] Mean (±standard deviation) of duplicate analysis.
[b] RDS, rapidly digestible starch; SDS, slowly digestible starch; RS, resistant starch.
[c] NC, NP, NL – unmodified corn, pea and lentil starches.
[d] Annealed (T_o−15 °C, 70% moisture, 24 h) corn (CA15), pea (PA15) and lentil (LA15) starches.
[e] Annealed (T_o−10 °C, 70% moisture, 24 h) corn (PA10), pea (PA10) and lentil (LA10) starches.
[f] Heat-moisture treated (100 °C, 30% moisture, 2 h) corn (CH100), pea (PH100) and lentil (LH100) starches.
[g] Heat-moisture treated (120 °C, 30% moisture, 2 h) corn (CH120), pea (PH120) and lentil (LH120) starches.

interactions may have been those that were formed between AM–AM chains during ANN and HMT (AM–AM interactions being much stronger than those between AMP–AMP and/or AM–AMP would be disrupted only at very high temperatures).

3.7. Expected glycemic index (eGI)

The eGI of native, ANN, and HMT starches before and after gelatinization are presented in Figs. 6a and b, respectively. The eGI of

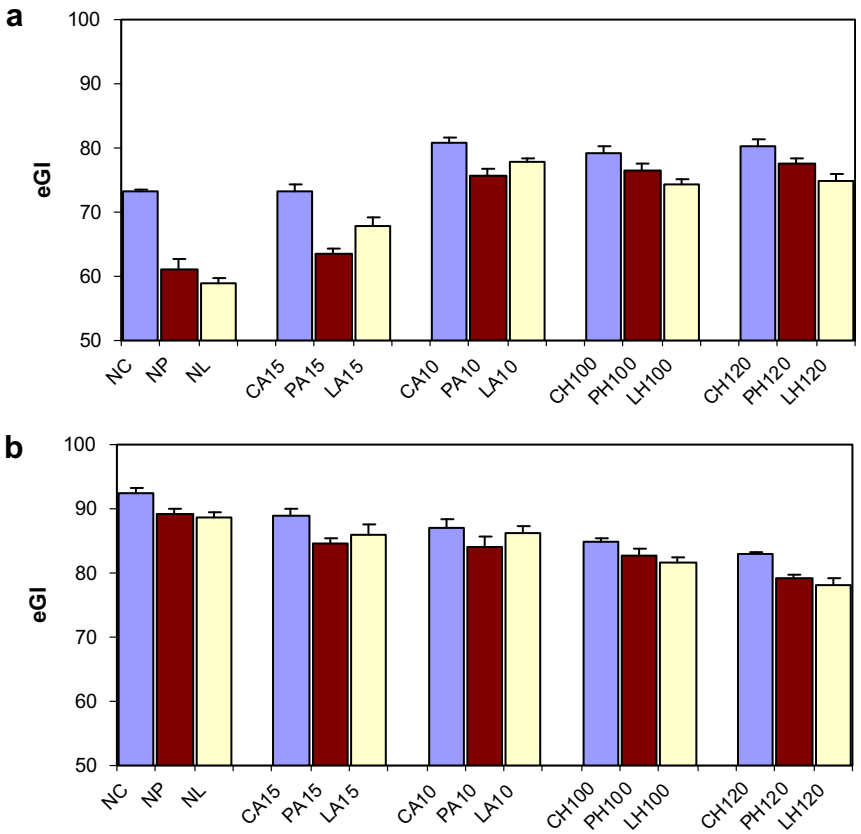

Fig. 6. Expected glycemic index (eGI) of corn, pea and lentil starches subjected to annealing and heat-moisture treatment in their granular form (a) and after gelatinization (b). CA10, PA10, LA10 and CA15, PA15, LA15 represent corn, pea and lentil starches annealed for 24 h at 10 and 15 °C below the onset (T_o) temperature of gelatinization, respectively. CH100, PH100, LH100 and CH120, PH120, LH120 represent corn, pea and lentil starches heat-moisture treated at 30% moisture for 2 h at 100 and 120 °C, respectively.

native granular corn starch was much higher (73.2) than that of pea (61.2) and lentil (58.8) starches. This could be attributed to the higher proportion of short A chains (DP 6–12) in corn starch (discussed earlier). ANN and HMT significantly increased (Fig. 6a) eGI in all granular starches. The extent of this increase was more pronounced at T_o-10 °C (ANN) and at 120 °C (HMT). The increase in eGI on ANN and HMT of the granular starches followed the order: lentil > pea > corn (Fig. 6a). Gelatinization increased eGI significantly in all starches (Fig. 6b). The extent of this increase followed the order: lentil > pea > corn (Fig. 6b). ANN and HMT decreased eGI values of all gelatinized starches. The extent of this decrease was more pronounced at T_o-10 °C (ANN) and at 120 °C (HMT). The eGI values of HMT gelatinized starches were lower than those of the ANN gelatinized starches (Fig. 6b). As discussed earlier, AM–AM interactions, formed during ANN and HMT, are not disrupted during gelatinization. This would decrease starch chain accessibility to hydrolyzing enzymes, thereby decreasing eGI.

4. Conclusions

The physicochemical properties of pea and lentil starches differed from those of corn starch with respect to amylose content, amylopectin chain length distribution, amylose leaching, granular swelling, gelatinization transition temperatures and enthalpy, and RDS and RS levels. Starch susceptibility to enzyme digestion is substantially influenced by physical modification (ANN and HMT). In granular native starch, the RDS and RS contents increased but SDS content decreased on ANN and HMT. HMT resulted in a greater change on RDS, RS and SDS levels than ANN. The increase in RS on ANN and HMT reflects enhanced interactions between starch chains, and perfection of some already existing crystallites. However, in gelatinized starch, ANN and HMT induced the decrease in RDS content, and the increase in SDS and RS contents. HMT is better suited for increasing thermo-stable SDS and RS than ANN. The eGI of granular native starch increased on ANN and HMT, whereas that of gelatinized starch decreased. This change was more pronounced with increase in treatment temperature. The increase in thermo-stable SDS and RS, and decrease in eGI after gelatinization on ANN and HMT suggest that AM–AM interactions, which are formed during treatment, are not disrupted during gelatinization, resulting in restricted accessibility of starch chains to the hydrolyzing enzymes.

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