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COMPOSITION, THERMAL BEHAVIOR AND GEL TEXTURE OF PRIME AND TAILINGS STARCHES FROM GARBANZO BEANS AND PEAS

Abstract

Prime and tailings starches of garbanzo beans and peas were separated and their chemical composition, physical properties, thermal behavior and gel properties were determined. Starch granules smaller than 35μm was 85% in garbanzo beans, 66.8% in a smooth pea cv. Latah and only 18.4% in a smooth pea cv. SS Alaska. Amylose content of prime starch was 35.9% in garbanzo beans, 44.5% to 48.8% in smooth peas and 86.0% in wrinkled pea cv. Scout. Tailings starch had a higher amylose content by at least 8% than its corresponding prime starch. The endothermic enthalpy value of garbanzo bean and two smooth pea prime starches ranged from 12.1 to 14.2 J/g, while prime starch from wrinkled peas gave a distinctly lower enthalpy value of 1.1 J/g. Differential scanning calorimetry endothermic enthalpy and amylograph pasting properties of prime starch were significantly related to its amylose content ($P<0.05$). Prime starches of garbanzo beans and smooth peas produced highly cohesive elastic gels. Wrinkled pea prime starch formed the strongest, though brittle, gel, as indicated by high hardness (21.8 N), low cohesiveness (0.29) and low springiness (0.82). Hardness of gel stored at 22°C and at 4°C was positively correlated with amylose content of starch.

Introduction

Legumes have been consumed traditionally as whole seeds or as a ground flour after dehulling. The rapidly growing food industry constantly demands new ingredients, which has drawn the attention of researchers to legume components obtained by the wet fractionation process (Schoch and Maywald 1968, Czuchajowska and Pomeranz 1994). At present there is a strongly visible public interest in natural, unmodified sources of food ingredients. For example, unmodified starch is gaining attention because labeling a food product as "natural" is attractive to consumers. The fractionation of legumes into their main components (starch, protein and fiber) is one way to increase the value of legumes by

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broadening their application. These legume fractions could be used to supplement non-legume food products to improve their textural and nutritional value.

The purposes of this study were: to evaluate the chemical composition and thermal behavior of prime and tailings starches obtained from garbanzo beans and smooth and wrinkled peas; to determine size distribution of prime starch granules by image analysis; to examine the physical properties of prime and tailings starch gels during storage at different temperatures; and, to relate chemical composition of starches to textural properties of gels.

Materials and methods

Materials

Garbanzo bean flour, stone milled from split or broken seeds, was provided by Blue Mountain Seeds, Inc. (Walla Walla, WA). One smooth pea, cv. Latah, was obtained from Dr. F. Muehlbaur, ARS-USDA, Pullman, WA. A second smooth pea, cv. SS Alaska, and a wrinkled pea, cv. Scout, were purchased from Crites Co. (Moscow, ID).

Preparation of starch

Garbanzo bean flour, with particle size smaller than 86 μm, and pea flours, a blend of three breaks and first reduction, were fractionated into prime starch, tailings starch and water solubles according to the method of Otto et al (1997a).

Chemical characteristics of isolated legume starches

Protein content (N x 6.25) of both prime and tailings starches was determined by a Leco instrument (Leco Corp., St. Joseph, MI) equipped with a thermoconductivity detector. Moisture content was determined by oven-drying for 1 hr at 130 °C (AACC Method 44-15A 1995), ash by dry combustion for 16 hr at 580°C (AACC Method 08-01, 1995) and free lipids by petroleum ether extraction, followed by evaporation to constant weight under vacuum (AACC Method 30-25 1995). Insoluble and soluble dietary fiber were determined by the procedure of Prosky et al (1988). Starch content was determined after its enzymatic conversion to glucose by successive treatment with α-amylase, protease and amyloglucosidase (Prosky et al 1988). The released glucose was measured with the glucose oxidase-peroxidase reagent (Lloyd and Whelan 1969). Amylose content of starch was determined by the procedure of Knutson and Grove (1994).

Physical properties of starch

The size distribution of the garbanzo bean and smooth pea starches was determined by image analysis. The granule image was transferred from an Olympus BH-2 photo microscope to a Quadra 950 Macintosh computer via a Pulnix BW CCD camera (Pulnix, Sunnyvale, CA). Each image was analyzed by NIH Image Analysis version 1.52 (Bethesda, MD) and converted to micrometers. Five hundred granules of each starch were measured by free-hand circling on the computer screen.

Differential Scanning Calorimetry (DSC)

DSC characteristics of starches were determined with a DSC-4 instrument (Perkins-Elmer Corp., Norwalk, CT). An indium standard was used for temperature and enthalpy calibration. A 10 mg sample and 20 µl of distilled water were placed in a stainless steel capsule, sealed and allowed to equilibrate for 30 min at room temperature. The sample was then heated from 20°C to 180°C at a rate of 10°C per min. A capsule with inert material (Al_2O_3) and water served as the reference sample. For each endothermic curve, temperature of transition onset, peak and completion were determined by data processing software. The transition enthalpy was calculated from the peak area by software and expressed as joules per gram (J/g) of dry matter.

Amylograph

Pasting properties of starch were determined with a Brabender amylograph by a modification of the method of Shuey and Tipples (1980).

Starch gel texture

Starch slurry in distilled water (8%) was prepared and heated at a rate of 1.5°C/min to 93.5°C using the Brabender viscoamylograph and held at that temperature for 10 min. The paste was then poured into eight individual cylindrical stainless steel molds (3.5 cm height and 3.5 cm inside diameter). Gels for wrinkled pea starch were prepared by autoclaving starch slurry (8%) at 126°C for 1 hr. Duplicate gels were stored for 24 hr and 72 hr at 22°C and 4°C. The gels to be stored for 72 hr at 22°C were vacuum packaged in gas impermeable plastic bags to minimize microbial growth.

The gel texture was then evaluated at least in duplicate by texture profile analysis (TPA) using the TA-XT2 Texture Analyzer (Stable Micro Systems, Haslemeres, England). Each cylindrical gel was placed upright on a metal plate and compressed at a rate of 1.0 mm per sec to 30% of its original height using a 5 cm diameter metal disk. The compression was repeated twice to generate a force-time curve from which hardness (height of the first peak) and springiness (ratio between recovered height after the first compression and the original gel height) were determined. Cohesiveness was calculated as the ratio between the area under the second peak and the area under the first peak (Bourne 1968, Friedman et al 1968).

Statistical analyses

All physical and chemical measurements of samples at each treatment were performed at least in duplicate. Analysis of variance (ANOVA) and least significant differences (LSD) were calculated by the Statistical Analysis System (SAS, 1986). Significance was defined at the 5% level.

Results and discussion

Characteristics of starches

Chemical compositions of both prime and tailings starches separated from garbanzo beans and peas are summarized in Table 1. Starch content of prime starch determined by enzymatic assay ranged from 97.5% in the wrinkled pea cv. Scout to 99.4% in the smooth pea cv. SS Alaska. Protein and ash contents of prime starches from garbanzo beans and smooth pea cvs. Latah and SS Alaska were lower than 0.35% and 0.19%, respectively, indicating that isolated starches were very pure. The prime starch of wrinkled pea cv. Scout had significantly higher protein (0.96%) and ash (0.31%) content than did the prime starch from garbanzo beans and smooth peas. This result could be explained by the difficulty in the fractionation process of wrinkled pea cv. Scout due to its high fiber content and composite starch granules (Otto et al 1997a).

Table 1

Characteristics of prime and tailings starches from garbanzo beans and peas[a]

Starch	Starch (%)	Protein[b] (%)	Ash (%)	Total Fiber (%)	Amylose (%)
Prime Starch					
Garbanzo Bean	99.1	0.17	0.17	trace	35.9
Smooth Pea					
cv. Latah	99.0	0.33	0.01	trace	44.5
cv. SS Alaska	99.4	0.35	0.08	trace	48.8
Wrinkled Pea					
cv. Scout	97.5	0.96	0.31	trace	86.0
LSD	0.66	0.28	0.01	...	0.54
Tailings Starch					
Garbanzo Bean	38.5	7.22	2.08	51.9	49.1
Smooth Pea					
cv. Latah	64.8	7.61	1.29	26.2	52.6
cv. SS Alaska	63.2	4.55	1.37	30.6	57.0
Wrinkled Pea					
cv. Scout	45.1	10.20	1.21	43.1	94.0
LSD	0.42	1.19	0.11	0.69	0.75

[a]Results expressed on a dry weight basis.

[b]N x 6.25.

Contrary to the high purity of prime starches, tailings starches from garbanzo beans and peas contained considerable amounts of protein, ash and fiber. The starch content of isolated tailings starches was over 63.2% in the two smooth peas, 45.1% in wrinkled pea cv. Scout and 38.5% in garbanzo beans. The protein content of tailings starches ranged from 4.6% to 10.2%, ash from 1.21% to 2.08% and fiber from 26.2% to 51.9%. The high concentration of these components indicates that tailings starches are a mixture of starch granules, cell wall materials and insoluble proteins.

Amylose content was 35.9% for garbanzo bean prime starch, 44.5% for cv. Latah and 48.8% for SS Alaska (Table I). Wrinkled pea cv. Scout had the highest amylose content (86.0%) in prime starch. Amylose content of tailings starch was always higher by at least 8% than that of prime starch in both garbanzo beans and pea cultivars. This can be explained by the large population of small-sized granules within the tailings starch. The smaller starch granules are typically higher in amylose than are larger granules (Szczodrak and Pomeranz 1991, MacGregor and Fincher 1993).

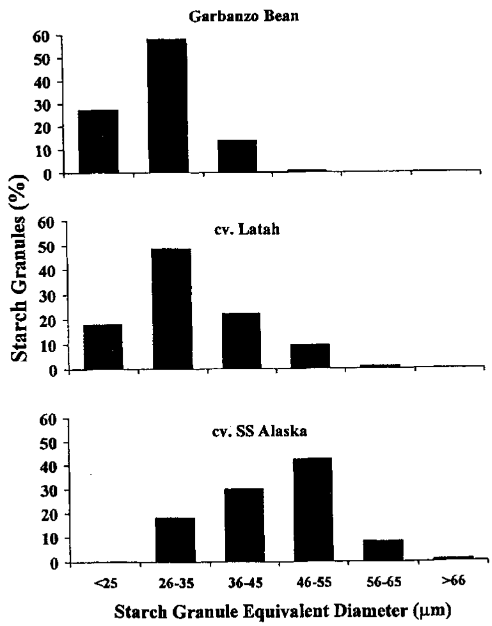

Fig. 1. Size distribution of prime starch granules from garbanzo beans and smooth pea cvs. Latah and SS Alaska determined by image analysis.

Size distributions of prime starch granules from garbanzo beans and the two smooth pea cultivars, determined by image analysis, are graphically presented in Figure 1. Garbanzo bean prime starch granules were smaller than those of smooth peas and ranged from 25 μm to 55 μm in diameter. Granules smaller than 35 μm represented 85% of total garbanzo bean starch. While granules smaller than 25 μm made up 27.2% in garbanzo bean starch, granules larger than 45μm were only 1%. Prime starch from cv. Latah represented a broader range of granule size than that from garbanzo beans, ranging from 25 μm to

65 μm, with a dominant granule size of 26–35 μm. Starch from cv. SS Alaska covered the broadest range of granule size, from 26 μm to greater than 66 μm, with 40% of the granules ranging from 46 to 55 μm. Distribution of starch granules from the wrinkled pea cv. Scout was not determined, as many of the compound granules were broken, leaving small granular pieces that were difficult to distinguish from the intact granules.

Thermal behavior of starches

The thermal behavior of prime and tailings starches was evaluated by DSC and amylograph tests. The DSC transition temperatures and enthalpy values of prime and tailings starches are given in Table 2. The onset temperature of prime starch of garbanzo beans did not differ significantly from that of smooth or wrinkled peas. However, the transition temperature of wrinkled pea starch was about 6°C higher than for garbanzo beans and the two smooth peas. Garbanzo beans had the highest endothermic enthalpy value of starch (14.2 J/g), followed by smooth pea cvs. SS Alaska (12.8 J/g) and Latah (12.1 J/g).

Table 2

Differential scanning calorimetry characteristics of prime and tailings starches from garbanzo beans and peas[a]

Starch	T_o[b] (°C)	T_p[c] (°C)	ΔH[d] (J/g)
Prime Starch			
Garbanzo Bean	62.8	68.1	14.2
Smooth Pea			
cv. Latah	62.1	68.6	12.1
cv. SS Alaska	61.4	67.7	12.8
Wrinkled Pea			
cv. Scout	62.4	74.7	1.1
LSD[e]	0.87	1.33	1.83
Tailings Starch			
Garbanzo Bean	60.5	73.2	1.5
Smooth Pea			
cv. Latah	58.0	69.5	5.4
cv. SS Alaska	56.6	67.2	4.6
Wrinkled Pea			
cv. Scout	70.9	86.8	0.8
LSD	2.26	3.45	1.22

[a]Values are averages of two replications.
[b]T_o = onset temperature.
[c]T_p = peak temperature.
[d]_H = transition enthalpy.
[e]Least significant difference (P = 0.05). Differences between two means exceeding this value are significant.

Prime starch of wrinkled pea cv. Scout gave the lowest enthalpy value of 1.1 J/g due to its high amylose content (86%). The highest enthalpy value of garbanzo bean starch was due to its high amylopectin content. Prime starches from the two smooth peas, which had a lower enthalpy value by at least 1.4 J/g than that of garbanzo beans, also had approximately 10% more amylose content (Table 1).

Transition enthalpies of tailings starches were significantly lower than those of corresponding prime starches. Several factors can explain the differences in enthalpy values between prime and tailings starches: total starch content (Table 1), size and mechanical damage of starch granules (Otto et al 1997b), amylose content (Table 1) and interactions between other tailings starch components. These differences in transition enthalpy between prime and tailings starches from garbanzo beans and peas are visualized by the size and shape of DSC enthalpy curves (Figure 2). Prime starches from garbanzo beans and smooth peas, consisting of pure and undamaged granules with at least 52% amylopectin, showed narrow and well defined endothermic peaks. Tailings starches contained small and damaged granules admixed with insoluble protein and fiber, and showed rather flat and broad DSC endothermic curves.

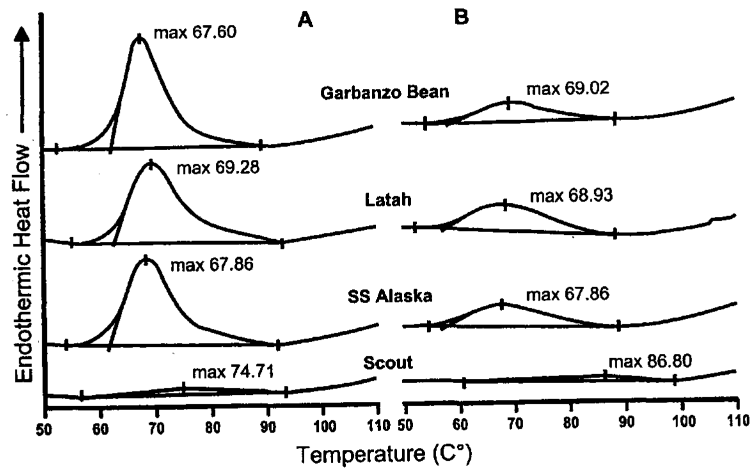

Fig. 2. Differential scanning calorimetry thermograms of prime starch (A) and tailings starch (B) from garbanzo beans, smooth pea cvs. Latah and SS Alaska and wrinkled pea cv. Scout.

Pasting characteristics of the legume starches, as determined by amylograph, are shown in Table 3. Prime starches of garbanzo beans and both varieties of smooth peas had similar patterns of pasting curves. Pasting viscosity at 93.5°C was 395 BU in garbanzo beans and 305 BU and 490 BU in the smooth pea cvs. Latah and SS Alaska, respectively. During 30 min holding at 93.5°C with constant shear, viscosity increased by over 70 BU. During the cooling period from 93.5°C to 50°C, set-back was extensive, as shown by the large increases in viscosity. Pasting viscosity further increased during the holding period at 50°C with constant shear. Wrinkled pea cv. Scout showed no viscosity development, as temperatures were not high enough for the starch granules to fully swell and gelatinize the granules.

Table 3

Amylograph pasting properties of prime and tailings starches from garbanzo beans and peas

Starch	Viscosity (BU)			
	at 93.5°C 0 min	at 93.5°C 30 min	at 50°C 0 min	at 50°C 30 min
Prime Starch				
Garbanzo Bean	395	495	740	800
Smooth Pea				
cv. Latah	305	377	655	750
cv. SS Alaska	470	540	910	1050
Wrinkled Pea				
cv. Scout	0	0	5	10
Tailings Starch				
Garbanzo Bean	80	170	218	200
Smooth Pea				
cv. Latah	370	455	595	575
cv. SS Alaska	255	337	417	405
Wrinkled Pea				
cv. Scout	5	5	18	18

Pasting properties of tailings starches from garbanzo beans and smooth peas were generally lower than corresponding prime starches and showed lower stability during the holding period at 50°C (Table 3). The higher viscosities of tailings starches from smooth pea cvs. SS Alaska and Latah than that of garbanzo beans could be due to their higher starch content. The viscosity development in the tailings starch of cv. Scout was due to protein and cell wall components, since starch did not contribute to any viscosity as shown in prime starch (Table 3).

Characteristics of starch gels

The TPA parameters, hardness, cohesiveness and springiness of starch gels varied broadly among starches within each storage temperature (Table 4). Hardness of prime starch gels, an important textural parameter reflecting the strength of gel, was 7.9 N in garbanzo beans, 11.4 N in cv. Latah and 11.1 N in cv. SS Alaska, when stored at 22°C. The prime starch gel of wrinkled pea cv. Scout showed a significantly lower hardness value of only 0.98 N because of incomplete gelatinization of starch at 93.5°C. However, when the prime starch slurry of cv. Scout was autoclaved at 126°C for 1 hr, a strong gel with a hardness value of 21.8 N was formed. The hardness of gels stored at 4°C followed the same pattern as those stored at 22°C. However, due to facilitated retrogradation at 4°C, the hardness of gels increased by 3.8 N for garbanzo beans, 5.3 N for smooth pea cv. Latah, 8.4 N for cv. SS Alaska and 4.7 N for autoclaved starch of wrinkled pea cv. Scout. A strong positive correlation was obtained between amylose contents and hardness of gels. Correlation coefficients were 0.965 for gels stored at 22°C and 0.967 for gels stored at 4°C. Cohesiveness, which reflects gel structure, was highest in garbanzo beans (0.95), followed by cv. SS Alaska (0.91) and cv. Latah (0.88). Storing gels at 4°C did not significantly affect cohesiveness. The lowest gel cohesiveness value (0.29) for cv. Scout indicated that the gel was very strong but brittle. Springiness of gels from garbanzo beans and smooth peas was over 0.96, indicating high recovery of gel height after first compression. Gels from cv. Scout showed a much lower springiness value than others, as could be expected from its low cohesiveness value.

Table 4

Texture profile analysis parameters of prime starch gels stored at 22°C and 4°C for 24 hrs[a]

Starch sample	Hardness (N)		Cohesiveness (ratio)		Springiness (ratio)	
	22°C	4°C	22°C	4°C	22°C	4°C
Garbanzo Bean	7.90	11.7	0.95	0.94	0.99	0.98
Smooth Pea						
cv. Latah	11.4	17.7	0.88	0.84	0.96	0.95
cv. SS Alaska	11.1	19.5	0.91	0.85	0.98	0.97
Wrinkled Pea						
cv. Scout	0.98	1.10	0.39	0.43	0.66	0.64
cv. Scout (AC[b])	21.8	26.5	0.29	0.29	0.82	0.76
LSD[c]	0.96	1.35	0.05	0.03	0.02	0.04

[a]Gels contain 8% starch on a dry weight basis.
[b]Autoclaved at 126°C for 1 hr.
[c]Least significant difference (P=0.05). Differences between two means exceeding this value are significant.

The increase in hardness due to accelerating retrogradation during storage at 4°C for all legume prime starch gels is shown graphically in Figure 3. Statistically significant increases in gel hardness were obtained for all gels by extending storage from 24 hr to 72 hr.

Gel hardness of tailings starches from smooth and wrinkled peas stored at 22°C and 4°C for 24 and 72 hr are shown in Figure 4. Garbanzo bean tailings starch, containing less than 40% starch, did not form a gel. The large differences in composition of tailings starches originating from different legumes (Table 1) make it difficult to compare gel texture. The hardness of tailings starch gels stored at 4°C was higher than for those stored at

22°C. Storage time also had a significant effect on gel hardness (except cv. Latah). These changes in hardness due to storage temperature and time indicate that starch plays an important role in the textural properties of tailings starch gel.

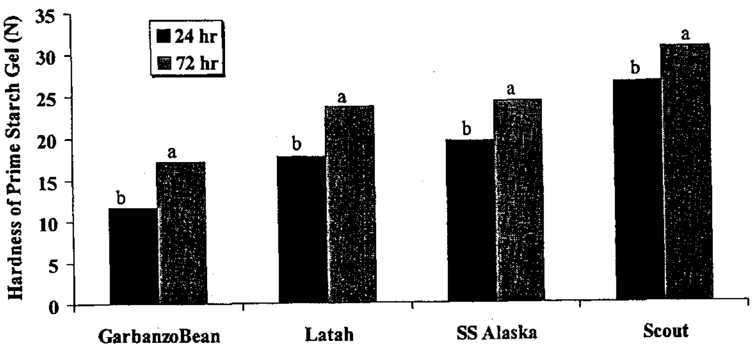

Fig. 3. Hardness of prime starch gels from garbanzo beans, smooth pea cvs. Latah and SS Alaska and wrinkled pea cv. Scout stored at 4°C for 24 and 72 hr. Gels for each legume starch were prepared by heating to 93.5°C for 10 min, except cv. Scout, which was prepared by autoclaving at 126°C for 1 hr. The letters at the top of each bar indicate significant differences at the 5% level.

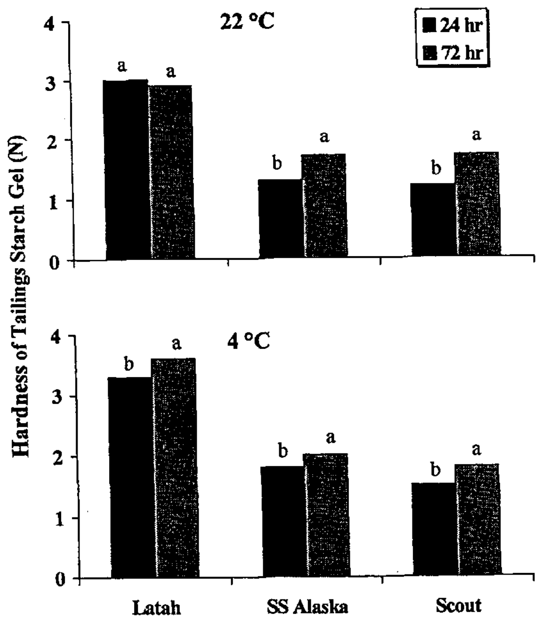

Fig. 4. Hardness of tailings starch gels from smooth pea cvs. Latah and SS Alaska and wrinkled pea cv. Scout stored at 22°C and 4°C for 24 and 72 hr. Gels for each legume tailings starch were prepared by heating to 93.5°C 10 min, except cv. Scout, which was autoclaved at 126°C for 1 hr. The letters at the top of each bar indicate significant differences between storage times at the 5% level.

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STRUKTURA I FUNKCJONALNOŚĆ SKROBI JĘCZMIENNYCH

Streszczenie

Zawartość amylozy w zwykłych i wysoko amylozowych skrobiach jęczmiennych oznaczono metodą kolorymetryczną. Ustalono, że wynosi ona odpowiednio 24,6 i 48,7%, natomiast w skrobi woskowej znaleziono zaledwie ślad (0,04%) amylozy. Amylopektyna pozbawiona rozgałęzień izoamylazą mało różniła się od zwykłych i wysoko amylozowych skrobi jęczmiennych, podczas gdy amylopektyna z woskowej skrobi jęczmiennej miała wyraźnie mniej, bo 45%, frakcji o wysokim stopniu spolimeryzowania (DP < 15).

Skrobia woskowa, normalna i wysoko amylozowa miały różne dyfraktogramy proszkowe. Skrobia woskowa wykazywała ostrzejsze piki przy 0,58; 0,51; 0,49 i 0,38 nm niż skrobia zwykła i i wysoko amylozowa. Odstęp *d* przy 0,44 nm charakteryzujący kompleksy amylozowo-lipidowe był najwyraźniejszy w przypadku skrobi wysoko amylozowej i nie pojawiał się w widmach skrobi woskowej.

Termogramy DSC skrobi zwykłej i wysoko amylozowej miały dwa wyraźne piki przy 60°C odpowiadający kleikowaniu skrobi i powyżej 100°C dotyczący kompleksu amylozowo-lipidowego. Skrobia z jęczmienia woskowego dawała tylko jeden endotermiczny pik kleikowania amylopektyny o entalpii 16,0 J/g.

Retrogradacja skrobi skleikowanej trzech typów jęczmienia przechowywanej w 4°C pokazała, że szybkość rekrystalizacji amylpektyny ze skrobi zwykłej i wysoko amylozowej była porównywalna gdy entalpię rekrystalizacji obliczano na procentową zawartość amylopektyny. W skrobi woskowej nie zaobserwowano piku rekrystalizacji amylopektyny.

Czas przechowywania miał duży wpływ na rekrystalizację amylopektyny. Entalpia dla zwykłej skrobi wzrosła z 1,93 J/g po 24 h przechowywania do 3,74 J/g po 120 h. Gdy żel mieszano co 24 h entalpia wyraźnie spadała.

Stwierdzono wysoce statystycznie istotną korelację (r = 0,991) między parametrami DSC retrogradowanej skrobi zwykłej i twardościa żeli z niej. Korelacja między entalpiami i twardością żeli wskazuje, że struktura żelu zależała przede wszystkim od struktury i funkcjonalności skrobi. Zależność między właściwościami skrobi i stężeniem skrobi może powodować, że przy produkcji pożądanych kleików korzystniejsze będzie operowanie stężeniem skrobi bez konieczności stosowania frakcjonowania skrobi na mokro.