KOREAN J. FOOD SCI. TECHNOL.
Vol. 9, *No.* 2 (1977)

Physicochemical Properties of Buckwheat Starch

by
S.K. Kim, T.R. Hahn, T.W. Kwon and B.L. D'Appolonia*

Food Resources Lab., Korea Institute of Science and Technology, Seoul
*North Dakota State University, Fargo, North Dakota, U.S.A.**

(Received March 25, 1977)

메밀 전분의 이화학적 성질에 관한 연구

김성곤 · 한태룡 · 권태완 · 비 엘 다포로니아*

한국과학기술연구소 식량자원연구실
노스다코타주립대학교 곡류이공학과*

(1977년 3월 25일 수리)

Abstract

Physicochemical properties of buckwheat starch were investigated. Starch granules were in the range of 4.3~11.4 microns in size, the average being 7.8 microns. The starch had a water-binding capacity value of 103.7%, blue value of 0.35 and amylose content of 25%. The initial and final gelatinization temperatures were 61° and 65°C, respectively. Amylograph data showed that the starch had an initial pasting temperature of 64.5°C. The kinetic study of crystallization of buckwheat starch during aging at 21°C suggested that the mechanism of starch crystallization is instantaneous nucleation followed by rod-like growth of crystals.

Introduction

Buckwheat(*Fagpyrum esculentum* Moench) is not a true cereal. It belongs to the *Polygonaceae* family but,like the cereals, the grain of buckwheat is a dry fruit.[1] The black hulls of the fruit are not suited for human food. Structurally, they have little in common with the bran coat of cereals. The seed proper (groat) is similar to that of cereals in that it consists of starchy endosperm and oily embryo.[1]

It is known[2] that buckwheat is the best known source of proteins of high biological value in the plant kingdom, having 92.3% of the value of nonfat milk solids and 81.4% of whole egg solids. Buckwheat proteins are particularly rich in lysine(6.0%) and contain less glutamic acid and proline and more arginine and aspartic acid than cereal proteins.[1,3,4]

However, very little attention has been given to the properties of buckwheat starch. The only information available is that of Hurusawa[6-9] who studied the physicochemical properties of starches from summer- and autumn-harvested buckwheat. Buckwheat flour has been utilized as human food in Korea in the form of noodles and "mook" (a gel of similar texture to jello). However, little knowledge is available on local buckwheat. The purpose of this study was to investigate the physicochemical properties of starch from local buckwheat and to examine the kinetics of retrogradation of buckwheat starch using the theory of Avrami.[10-12]

The Avrami theory has been widely applied to the crystallization of high polymers and has been shown to apply most accurately to the initial stages of the crystallization when the nuclei are forming and growing. Recently, it was shown that the kinetics of the crystallization process of wheat[13-15] and tapioca[16] starches could be represented by the Avrami equation.[10-12]

The Avrami equation is represented by

$$\theta=\exp(-kt^n) \quad \cdots\cdots (1)$$

where θ is the fraction of uncrystallized material remaining after time t, k is a rate constant and n is an integer varying from 1 to 4 and characteristic of the mode of nucleation(Table 1).

If the the elastic modulus of buckwheat starch gels (E), which is expressed as hardness is a linear measure of the extent of crystallization, then Eq.(1) can be expressed by

$$\theta=(E_L-E_t)/(E_L-E_o)=\exp(-kt^n) \quad \cdots\cdots (2)$$

Thus,

$$\log[-\log_e(E_L-E_t)/(E_L-E_o)]=\log k+n \log t \quad \cdots (3)$$

where E_o and E_t are the modulus at time O and t, respectively, E_L is the limiting modulus after a theoretical infinite time. The Avrami exponent(n) can be obtained from the gradient of the line and the rate constant(k) from the intercept by plotting $\log[-\log_e (E_L-E_t)/(E_L-E_o)]$ against $\log t$. When $n=1$ the best value for the rate constant can be determined from a graph of $\log_e(E_L-E_t)$ against t.[13] The reciprocal of the rate constant is termed time constant ($1/k$).

Table 1. Values for the Avrami exponent for various types of nucleation and growth[17]

n	Types of nucleation and growth
3+1=4	Spherulitic growth from sporadic nuclei
3+0=3	Spherulitic growth from instantaneous nuclei
2+1=3	Disc-like growth from sporadic nuclei
2+0=0	Disc-like growth from instantaneous nuclei
1+1=2	Rod-like growth from sporadic nuclei
1+0=1	Rod-like growth from instantaneous nuclei

n is a combined function of the number of dimensions in which growth takes place, and the order of the time dependence of the nucleation process (0 or 1).

Materials and Methods

Materials: Commercially milled buckwheat flour was obtaind from the Animal Feed Stuffs Laboratory of the Korea Institute of Science and Techology.

Starch Preparation: Buckwheat flour was suspended in water, blended for 5 min in a Waring blendor and passed through a 270-mesh sieve. After centrifugation at 3,000×g for 10 min, the starch at the bottom of centrifuge tube was recovered and reslurried in water followed by centrifugation. The starch was then suspended in Na OH solution, adjusted to pH 11.0, stored at 4°C over night and the supernatant was decanted. This alkali treatment was repeated once again. The starch recovered after centrifugation was washed with water until neutral, air dried and passed through an 80-mesh sieve.

Photomicrographs: The starch was suspended in 50% glycerol solution to give a 5% starch concentration and stained with 0.02% iodine solution prior to photomicroscopic examination.

Photomicrographs were achieved under normal and polarized light using an Olympus photomicroscope(Olympus Co., Japan) with a 700X magnification.

Starch Fractionation: Prior to fractionation, the starch was defatted with methanol in a Soxhlet extractor for 24hr, air dried and passed through an 80-mesh sieve.

The procedure used for starch fractionation was that of Montgomery and Senti.[18]

Amylose Determination: The colorimetric proceduredureof Williams *et al.*[19] was used for estimating amylose content.

Blue Value: Blue values of starch and its fractions at 680nm were determined by the method of McCready and Hassid.[20]

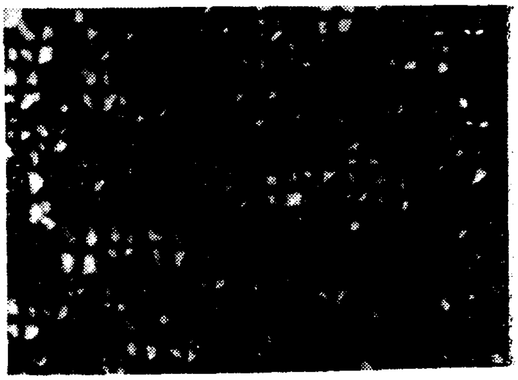

Fig. 1. Photographs of buckwheat starch under normal(left) and polarized light (right).

Water-Binding Capacity: The procedure followed was that of Medcalf and Gilles.[21]

Swelling Power: The swelling power over a range of temperatures was determined according to the procedure of Schoch.[22]

Gelatinization Temperature: Gelatinization temperature ranges were followed by observing loss of birefringence using a polarizing microscope equipped with a Kofler hot stage as described by Schoch and Maywald.[23]

Pasting Properties: Pasting propertie of starch were investigated with the Brabender Amylograph. A complete description of the procedure used was given by Medcalf and Gilles.[24]

Periodate Oxidation: Amylopectin fraction was oxidized with sodium metaperiodate using the procedure of Shasha and Whistler.[25]

Aging of Starch Gels: Starch gels were prepared as described previously.[15] At 0, 1, 2, 3 and 4 days, the hardness of the gels stored at 21°C was examined by a Texturometer (General Food Co., U.S.A.), with 20 measurements being made on each gel and an average taken. The limiting modulus was obtained from the gel stored at 2°C for 6 days. The hardness data were analyzed according to the Avrami equation.

Other Analyses: AACC official methods[26] were utilized for moisture, ash and protein determinations.

Results and Discussion

Starch Granules

Fig. 1 shows photographs of buckwheat starch granules under normal and polarized light. The granules were polygonal similar to those of rice.

The size of the granules ranged from 4.3 to 11.7 microns, the average being 7.8 microns, showing a somewhat lager granule size than rice starch (1.6—8.7 microns).[27]

Chemical and Physicochemical Properties

Chemical and physicochemical data for the buckwheat starch are summarized in Table 2. The starch had 12.0% moisture, 0.13% ash and 0.4% protein. It had a water-binding capacity of 103.7%. The intial and final gelatinization temperatures were 61° and 65°C, respectively. The amylose content was 25.0%, which is in good agreement with reported values of 23.8—25.8%[8] and 25.2%[19] that were based on the amperometric method. Blue values for starch, amylose and amylopectin were 0.35, 1.38 and 0.24, respectively. The blue value for the starch (Table 2) agrees with that of Hurusawa and Miyashita.[8]

Data on swelling power over a range of temperatures are shown in Table 3. The swelling powers at 30° and 50°C were 2.05 and 2.18, respectively. These results indicate that little swelling occurs at temperatures below 50°C. It has been postulated[29] that the bonding forces within the starch granule would influence the manner of swelling. Thus, a highly associa-

-ted starch with an extensive and strongly bonded micellar structure should be relatively resistant toward swelling. The swelling power values at 60°C indicate that a greater resistance toward swelling of buckwheat starch compared to the wheat and rye starches (Table 3). However, the swelling power value for buckwheat starch at 70° and 90°C was considerably higher than that for wheat and rye starches. The values for swelling power at higher temperatures represent progressive relaxation of the bonding forces within the granules.[28]

Table 2. Chemical and physicochemical data for buckwheat starch

Moisture (%)	12.0
Ash (%)	0.13
Protein(%)	0.4
Water-binding capacity(%)	103.7
Gelatinization temperature (°C)	61—65
Amylose content(%)	25.0
Blue value	0.35

Table 3. Swelling power of buckwheat starch

Starch	Swelling power at		
	60°C	70°C	90°C
Buckwheat[a]	2.95	9.38	22.88
Wheat[28]	4.77	6.13	11.80
Rye[28]	5.47	6.64	15.16

a Present study

Pasting Properties

An amylograph curve for buckwheat starch is shown in Fig. 2. Results of starch paste viscosities are given in Table 4. The starch had an initial pasting temperature of 64.5°C, thereafter the viscosity increased sharply.

Data in Table 4 indicate that the starch paste viscosity observed in this study is considerably different from those reported by Hurusawa and Miyashita.[6,7] These differences seem to be due largely to the differences in the location and harvest time of the buckwheat[6,7] and partly to the differences in the method of starch preparation.

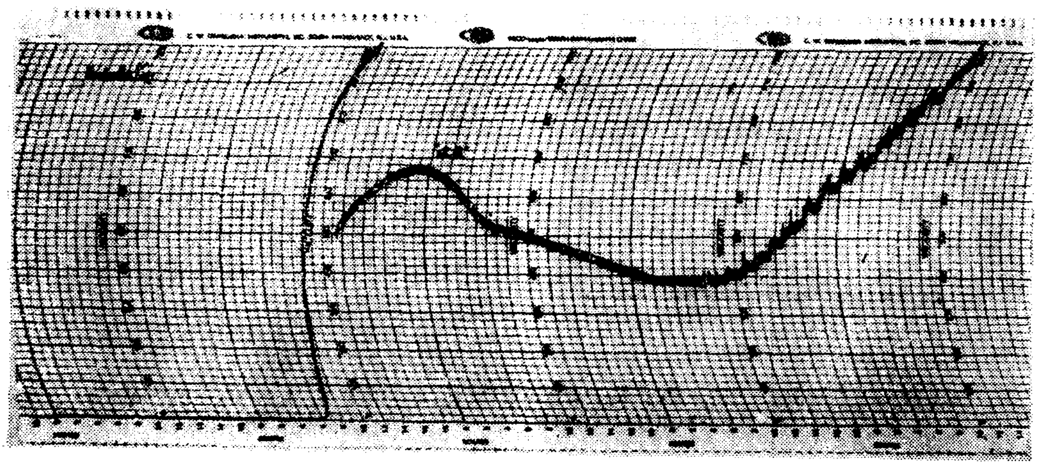

Fig. 2. An amylograph curve for buckwheat starch.

Table 4. Amylograph data on buckwheat starch

Starch	Pasting temperature (°C)	Peak height (BU)	Height at 92.5°C (BU)	10 min hold height (BU)	15 min hold height (BU)	Height at 50°C (BU)	Height at 30°C (BU)
Bucawheat[a]	64.5	1,170	1,050	950	910	1,465	—
Buckwheat[6,7]	64.3～68.7	530～1,030	530～990	600～970	—	—	1,510～2,440

a Present study

Aging of Starch Gels

Results of analyses of the Avrami eqation on the aging of the starch gels at 21°C are given in Fig. 3. The Avrami exponent was 0.94. Thus, within experimental error, the value for n was unity and this value was used for plotting $\log_e (E_L-E_t)$ against t to obtain the rate constant(Fig. 4). The time constant calculated was 2.33 days (Table 5).

The value for the Avrami exponent(i. e., $n=1$) suggests that the mechanism of starch crystallization is instantaneous nucleation followed by rod-like growth of crystals (Table 1). The same mode of nucleation was found for wheat[13,14,15] and cassava[16] starch gels.

Some physicochemical properties of buckwheat, wheat and cassava starches are compared in Table 5. In a previous paper, it was suggested[16] that since the linear amylose molecules associate easily and therefore retrograde rapidly the lower amylose content of cassava starch could possibly explain the slower rate of retrogradation of cassava starch than that of wheat starch. However, the buckwheat starch had a lower value for the time constant compared to that of wheat starch even though the amylose content for both starches was about the same (Table 5). These results may imply that a factor other than the amylose content could possibly be involved in determining the rate of retrogradation of starch.

It was demonstrated[15] that both amylose and amylopectin fractions influence the retrogradation process of starch gels upon aging. Thus, the differences in the values for the time constant of buckwheat and

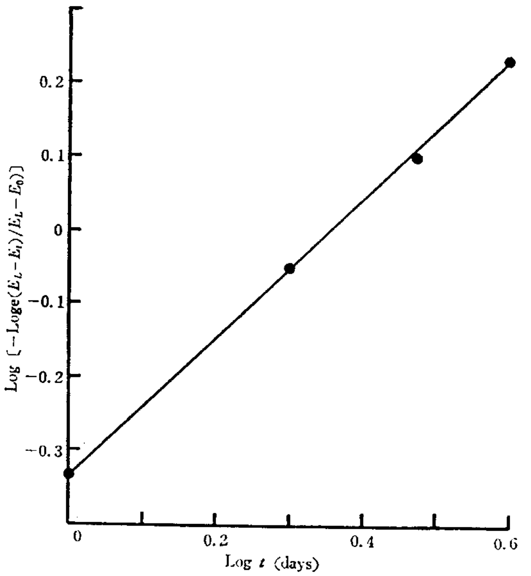

Fig. 3. Plot of log $[-\log_e (E_L-E_t)/(E_L-E_o)]$ agaist log t for 50% buckwheat starch gels stored at 21°C.

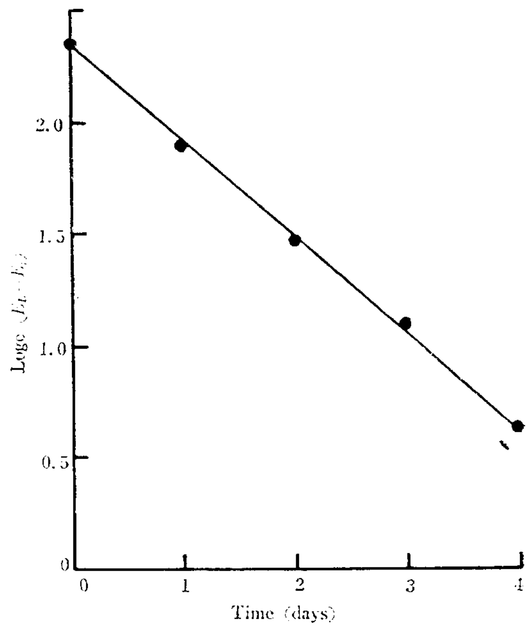

Fig. 4. Plot of $\log_e(E_L-E_t)$ against t for 50% buckwheat starch gels stored at 21°C.

Table 5. Comparison of physicochemical properties of buckwheat, wheat and cassava starches

Starch	Amylose content (%)	Amylopectin		Time constant of starch gels at 21°C (days)
		Branching (%)	Glucose units per segment	
Buckwheat[a]	25.0	4.0	25	2.33
Wheat [15,30]	24.5	4.4	23	3.80
Cassava[16,31]	18.6	—	21	11.60

a Present study

wheast starches (Table 5) could be due to the amylopectin. Since the amylopectin content for both starches is the same, it appears that differences in chemical properties of the amylopectin from buckwheat and wheat starches might affect the rate of retrogradation. The glucose units per segment for amylopectin from buckwheat starch was 25, whereas a value of 23 has been reported for wheat(Table 5). Thus, it may possible that the less branching and longer chain length per segment of buckwheat amylopectin compared to wheat amylopectin may facilitate the association between starch fractions (amylose-amylopectin and amylopectin-amylopectin) more easily than that between wheat starch fractions; resulting in a lower value for the time constant, that is, faster rate of retrogradation of buckwheat starch than wheat starch.

요 약

메밀 전분의 이화학적 성질을 살펴본바, 입자의 크기는 4.3—11.4 미크론(평균 7.8미크론)이었다. 전분의 물결합능력은 103.7%, 아밀로스 함량은 25%이었다. 복굴절성 소실의 측정법에 의한 호화개시 및 호화 종료 온도는 각각 61° 및 65°C이었고 아밀로그라프에 의한 초기 호화온도는64.5°C이었다. 전분의 노화속도는 21°C에서 밀 전분보다 다소 빨랐다.

References

1) Pomeranz, Y. and Robbins, G.S.: *J. Agr. Food Chem.*, **20**, 270(1972).
2) Sure, B. J.: *J. Agr. Food Chem.*, **3**, 793(1955).
3) Pomeranz, Y.: *Cereal Sci. Today*, **18**, 310(1973).
4) Pomeranz, Y., Marshall, H.G., Robbins, G.S. and Gilberston, J.T.: *Cereal Chem.*, **52**, 479(1975).
5) Hurusawa, Y. and Kobayashi, C.: *Eiyo To Shokuryo*, **15**, 436(1963).
6) Hurusawa, Y. and Kobayashi, C.: *Eiyo To Shokuryo*, **16**, 39(1964).
7) Hurusawa, Y. and Miyashita, S.: *Eiyo To Shokuryo*, **16**, 542(1964).
8) Hurusawa, Y. and Miyashita, S.: *Eiyo To Shokuryo*, **17**, 415 (1965).
9) Hurusawa, Y. and Miyashita, S.: *Eiyo To Shokuryo*, **18**, 381(1966).
10) Avrami, M.: *J. Phys. Chem.*, **7**, 1103(1939).
11) Avrami, M.: *J. Phys. Chem.*, **8**, 212(1940).
12) Avrami, M.: *J. Phys. Chem.*, **9**, 177(1941).
13) McIver, R.G., Axford, D.W. E., Colwell, K.H. and Elton, G.A.H.: *J. Sci. Food Agric.*, **19**, 560(1968).
14) Colwell, K.H., Axford, D.W.E., Chamberlian, N. and Elton, G.A.H.: *J. Sci. Food Agric.*, **20**, 550 (1969).
15) Kim, S. K. and D'Appolonia, B.L.: *Cereal Chem.*, **54**, 150(1977).
16) Kim, S.K., Ciacco, C.F. and D'Appolonia, B.L.: *J. Food Sci.*, **41**, 1249(1976).
17) Sharples, A.: *Introduction to Polymer Crystallization*, p. 50. Edward Anold Ltd., London (1966).
18) Montgomery, E.M. and Senti, F.R.:*J. Polymer Sci.*, **28**, 1(1958).
19) Williams, P.C., Kuzina, F.D. and Hlynka,I.:*Cereal Chem.*, **47**, 411(1970).
20) McCready, R.M. and Hassid,W.Z.: *J. Am. Chem. Soc.*, **65**, 1154(1943).
21) Medcalf, D.G. and Gilles, K.A.: *Cereal Chem.*, **42**, 558(1965).
22) Schoch, T.J.: *Method in Carbohydrate Chemistry*, ed. by R. L. Whistler, Vol. 4, p. 106. Academic Press: New York, N.Y. (1964).
23) Schoch, T.J. and Maywald, E.C.: *Anal Chem.*, **28**, 382(1956).
24) Medcalf, D.G. and Gilles, K.A.: *Staerke*, **4**, 101 (1966).
25) Schasha, B. and Whistler, R.L.: *Method in Carbohydrate Chemistry*, ed. by. R.L. Whistler, Vol. 4, p. 86. Academic Press: New York, N.Y. (1964).
26) American Association of Cereal Chemists: *AACC Approved Methods*. The Association: St. Paul, Minn. (1962).
27) Reyes, A.C., Albano, E.L., Briones, V.P. and Juliano, B.O,: *J. Agr. Food Chem.*, **13**, 438(1965).
28) Lorenz, K. and Hinze, G.: *J. Agr. Food Chem.*, **24**, 911(1976).
29) Leach, H.W., McCowan, L.D. and Schoch, T.J.: *Cereal Chem.*, **36**, 354(1959).
30) Berry, C. P., D'Appolonia, B.L. and Gilles, K.A.: *Cereal Chem.*, **48**, 415(1971).
31) Ciacco, F.: *Ph.D. Thesis*. North Dakota State University, Fargo, North Dakota, U.S.A.(1977).