Roles of Water-Soluble and Water-Insoluble Carbohydrates in the Gelatinization and Retrogradation of Rice Starch

Yoshiko Hibi, Hikone (Japan)

The roles of water-soluble carbohydrates leached from starch granule and water-insoluble ones left in starch granule in the gelatinization were studied relating to gel hardness in the retrogradation.
In the case of whole starch gel, hardness of rice starch gel was lower in the presence of lipids than it was in the absence of lipids, and an increase in hardness during storage at 5 °C was retarded by the presence of lipids. The characteristic of water-insoluble fraction paste of gelatinized normal rice starch was the opposite to that of whole starch gel. This seems to be due to the shortage of amylose in the paste.
When the proportion of amylose was high in the mixture of normal rice starch and waxy one, both the water-solubility and the gel hardness were strongly affected by lipids. On the contrary, the effects of lipids were hardly seen when the proportion of amylopectin was high in the mixed starches. Amylopectin of rice starch in the presence of amylose showed a considerable increase in complex formation.

1 Introduction

The texture and acceptability of starch-containing foods correlates with retrogradation of starch which has been made mainly described as the recrystallizing process of gelatinized starch. For breads added monoglyceride [1] or shortening oil [2, 3], retrogradation of bread is suppressed by the formation of helical complex of starch with lipids. In the previous study [4], starch-lipids complex affected the susceptibility to amylase, X-ray diffraction pattern, and water-solubility in the retrogradation process of cooked rice and normal rice starch paste.

Schoch [1] suggested that bread staling was due to the gradual association of amylopectin within the swollen granules, as differentiated from the leached amylose which had set up to a gel structure between granules immediately after baking. This means that amylose recrystallizes in a relatively early period of storage, but that amylopectin changes its state with time even after the earlier period. The latter is the long-term effect on recrystallization of starch that has been associated with changes in texture. *Miles* et al. [5] also reported the same view by measuring moduli of starch and amylose gels.

I have reported the relation between the viscoelastic properties of rice starch gel and the amount of water-soluble carbohydrate in the gelatinization with and without lipids [6].

On the other hand, the importance of insoluble amylose has been successively studied as correlation with rice quality, especially with textural parameter and sensory evaluation of cooked rice [7–12]. The presence of lipid decreases the amounts of carbohydrates solubilized from starch granules in the gelatinization [4, 6, 13–17], and the retrogradation of amylose differs from that of amylopectin [1, 5, 18].

In this study, the roles of water-soluble carbohydrates leached from starch granules and water-insoluble carbohydrates left in starch granule in the gelatinization were studied relating to gel hardness in the retrogradation.

2 Materials and Methods

2.1 Materials

Normal and waxy rice starches were supplied by Shimada Chemical Industry Co., Niigata, Japan. Palmitic acid was purchased from Kyoto Wako Pure Chemical Industry Co., Kyoto, Japan, and used without further purification.

2.2 Defatting of rice starch

Defatted normal rice starch and defatted waxy rice starch were prepared by Soxhlet extraction with 85 % methanol for 30 h. The amounts of the lipids extracted are shown in Table 1.

2.3 Reintroduction of lipids into defatted normal rice starch

Defatted normal rice starch (100 g) was suspended in 500 ml of methanol solution containing 18 g of palmitic acid which is the major fatty acid in rice starch [19, 20]. The mixture was refluxed for 5 h to introduce the lipids into the defatted starch. The starch was separated by filtration and dried after washing with ether. The amount of fatty acid reintroduced was 0.97 % (w/w) of the defatted starch.

2.4 Fractionation of amylose and amylopectin

Defatted normal and defatted waxy rice starches were dissolved at 1 % (w/v) in 1 N NaOH aqueous solution. After the solution was neutralized and heated to 90 °C, 10 ml of *l*-menthone [21] was added to produce a precipitate. After standing for 20 h at room temperature, three layers of supernatant, middle gel layer, and precipitate were obtained. The supernatant and middle gel layer were distinctively removed from the solution and precipitated by methanol. The separated precipitate of amylose-*l*-menthone complex and the precipitates obtained from supernatant and middle gel layer were dehydrated by ethanol, washed by ether, and air-dried.

The amounts of amylose and amylopectin are shown in Table 1. By iodine-staining reaction, middle gel layer was confirmed as amylopectin with longer chain than the chain of amylopectin in the supernatant (Table 1). Amylopectin used for the study of complex formation is extracted from the supernatant.

2.5 Gel permeation chromatography (GPC)

Starch (0.5 to 1.0 g) was suspended in 50 ml of water and heated by stirring at 85 °C for 30 min to obtain a gelatinized paste. Starch paste was centrifuged at 4000 rpm for 30 min. Total carbohydrates both in the supernatants and in the residues were analyzed by GPC under the following conditions [4]: column, 2.5×62 cm with Sepharose CL-2B gel, product

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Tab. 1. Starch composition.

Rice Starch	Lipid[a] (%)	Amylose[b] (%) (Blue Value)	Amylopectin (%) (Blue Value)		
			Total	I[c]	II[d]
Normal	0.65	21.8	78.2	52.0	26.2
		(1.23)	(0.23	0.24	0.18)
Waxy	0.16	3.0	97.0	46.9	50.1
		(1.16)	(0.17	0.21	0.12)

[a] Extracted by 85 % hot methanol.
[b, c, d] Precipitate, middle gel layer, and supernatant, respectively, obtained by adding *l*-menthone to defatted rice starch paste.

of Pharmacia Fine Chemicals Co.; eluant, 0.05 M NaOH aqueous solution; flow rate, 15 ml/h; temperature, 15 ~ 18 °C; elution volume of one fraction, 3 ml. Total carbohydrate in each fraction was measured by the phenol-sulfuric acid method [22] and a GPC elution pattern was drawn. The areas of the GPC elution patterns were normalized as to the amount of the total carbohydrates solubilized in the supernatants and as to the one in the residues which was calculated as 100.0 minus the amount of water-soluble carbohydrates. Then, the amounts of amylopectin and amylose were evaluated from the area of the elution pattern. From the previous results [4], the elution patterns showed that the carbohydrates were divided into two major fractions, namely, higher molecular weight and lower molecular weight fractions, respectively. The higher molecular weight fraction combined fractions no. 52 and below, and showed iodine staining color with λ_{max} of 580 nm (in 10^{-3} N I_2, 10^{-2} N KI solution). The lower molecular weight fraction, combining fractions above no. 52, had a color with λ_{max} of 620 nm. Molecular weight scale was calibrated using enzymatically synthesized amyloses [23].

2.6 Preparing of rice starch gel

Nondefatted (native), defatted and refatted normal rice starches were used to prepare starch pastes. 40 g of starch was suspended in 360 ml of water and heated by stirring in a boiling water bath for 10 min. Stirring rate was kept constant by electric stirrer. To prepare the gel consisted of only water-insoluble fraction of starches, the water-soluble fractions from the whole starch paste after gelatinization was removed; Water was added to hot paste, stirred, centrifuged at 4000 rpm for 30 min, and removed the supernatant. After repeating this procedure three times, water-insoluble fraction of whole starch paste was obtained.

Sixty grams of the paste with or without water-soluble fraction of starch was poured into vessels (60 mm diameter, and 28 mm height) and tightly sealed and stored at 5 °C for 5 days, after standing for 2 h at room temperature. Gel formation was visually monitored by self-supporting property [24] after taken from the vessel, and hardness of formed gel was measured.

2.7 Measurement of hardness of rice starch gel

Rheoner RE3305 model made by Yamaden Co., Tokyo, Japan, was employed for measuring hardness of rice starch gels, using the following conditions: thickness and diameter of sample, 20 and 60 mm, respectively; diameter of plunger, 16 mm; clearance, 10 mm ; compressing speed, 1 mm/s; temperature at measurement, 18 ~ 20 °C. For samples which did not form gel, the measurement was carried out for the samples in the vessels. Highest peak of the chart means hardness.

3 Results and Discussion

3.1 Effect of lipids on water-insolubility in the gelatinization of rice starch

In our previous GPC study [4], the water-soluble carbohydrate in the gelatinization without lipids much increased in all molecular weight fractions, even in amylopectin. In the present study, the water-insoluble carbohydrate in starch granules in the gelatinization was evaluated.

Fig. 1 shows the GPC elution patterns of water-insoluble carbohydrates in the residues of nondefatted (native), defatted, and refatted normal rice starch pastes which removed water-soluble carbohydrate in the supernatants. All elution patterns of the starch residues show one major peak of amylopectin and plateau of amylose. By defatting, the water-insoluble carbohydrates decrease in all molecular weight fractions, and in the refatted starch residue, although it is not obvious whether lipids were reintroduced as they were before defatting, the elution pattern returns to the one similar to that of native nondefatted starch.

Amounts of amylose and amylopectin in the water-insoluble fraction were calculated from the area of the elution pattern (Table 2). For nondefatted, defatted, and refatted rice starches, 10.4, 31.9, and 9.3 % of total carbohydrates, respectively, in the starch paste were solubilized. Hence,

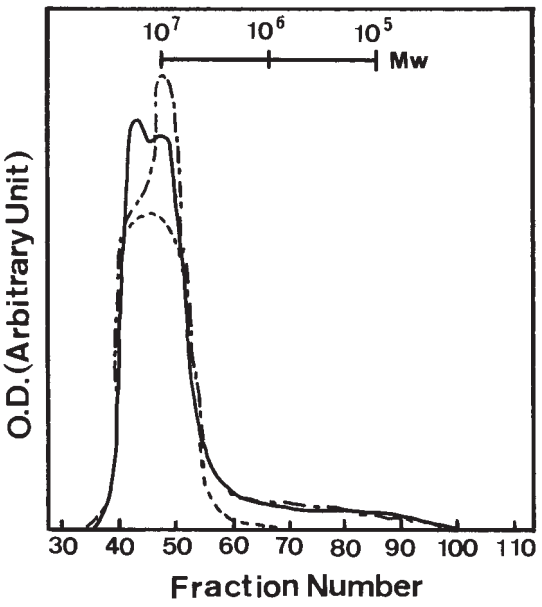

Fig. 1. Effect of lipids on the GPC elution patterns of the water-insoluble fractions of normal rice starch pastes.
Nondefatted (native) rice starch (——); defatted rice starch (– – –); refatted rice starch (–·–·–).

Tab. 2. Effect of lipids on water-insolubility in the gelatinization of rice starch.

Fraction	Water-Insoluble Carbohydrate (%)		
	Nondefatted	Defatted	Refatted
Total[a]	89.6	68.1	90.7
Amylose[b]	12.9	1.9	13.5
Amylopectin[b]	76.7	66.2	77.2

[a] 100.0 minus amount of water-soluble carbohydrate in the supernatant of starch paste.
[b] Calculated from the area of GPC elution patterns.

89.6, 68.1, and 90.7 % of total carbohydrates, respectively for nondefatted, defatted, and refatted rice starches are regarded as remaining in starch granules in the gelatinization. The results show a large amount of amylopectin (76.7 and 66.2 %, respectively, for nondefatted and defatted rice starches) and a small amount of amylose (12.9 and 1.9 %, respectively for nondefatted and defatted rice starches). This shows the opposite results in the proportions of amylose and amylopectin in the water-soluble carbohydrates of the supernatant [4], and by removing lipids, almost all amylose solubilizes in the gelatinization.

3.2 Hardness of rice starch gels with and without water-soluble fraction

Miles et al. [5] showed that on storage the short-term developments of gel structure and crystallinity were due to amylose within gel matrix, and long-term increase in the shear modulus of starch gel which was linked to a crystallization was due to amylopectin within starch granule embedded in an amylose gel matrix. This was the same view as mentioned by *Schoch* [1]. It is, hence, interesting to relate water-insoluble fractions in starch granules in the gelatinization to hardness of starch gel formed in the retrogradation. So, gels with and without water-soluble fraction of starch in the gelatinization were taken to measure hardness. No gel formation even after 5 days of storage was observed in the water-insoluble fraction of starch. Therefore, the fraction was actually the paste the hardness of which was measured within the vessel.

As shown in Table 3, before storage hardness of the whole starch gel increases by removing lipids and decreases by reintroducing lipid to defatted starch. On the contrary, for the paste of water-insoluble fraction of starch, hardness is naturally low, and it decreases by removing lipids and increases by reintroducing lipids to defatted starch.

Starch paste after gelatinization consists of solubilized carbohydrates almost all of which are amylose and of swollen starch granules or their fragments, and it exhibits viscoelastic properties. On cooling of concentrated starch paste, starch gel quickly develops; Solubilized carbohydrates form a continuous network which links swollen starch granules [25]. In the present study, swollen granules of water-insoluble fraction are not linked because of the lack of solubilized carbohydrates, and, hence, gel cannot be formed. As shown in Table 2 , almost all water-insoluble carbohydrate in the gelatinization with lipids is amylopectin, and the amount of amylose in the residue of starch granule decreases more by removing lipids.

Tab. 3. Effects of lipids and water-soluble carbohydrates on the hardness of rice starch gels.

($\times 10^3$ N/m^2)

Gel	Storage (day)	Starch		
		Nondefatted	Defatted	Refatted
Whole starch	0	2.93 ± 0.25[a]	9.35 ± 0.41	1.25 ± 0.10
	5	3.37 ± 0.27	10.43 ± 0.33	1.23 ± 0.31
	*[b]	1.15	1.12	0.98
Water-insoluble	0	0.37 ± 0.05	0.23 ± 0.04	0.73 ± 0.04
Fraction of starch[c]	5	0.57 ± 0.06	0.25 ± 0.02	0.96 ± 0.06
		1.54	1.09	1.32

[a] Mean ± SD (six measurements).
[b] Ratio of value observed after 5 days of storage to original one.
[c] No gel formation was observed, therefore, it was actually paste.

Gel hardness after storage was compared by ratio of value observed after 5 days of storage to original one (Table 3), because gels with and without water-soluble fraction were different from each other. In whole starch gel with and without lipids, hardness after 5 days of storage increased. Ratio of the change by storing was almost the same as that by removing lipids, but for refatted starch hardness after 5 days of storage was rarely changed, so increase of the hardness after storage may be suppressed in the presence of lipids. In water-insoluble fraction of starch, the hardness was low, especially in the absence of lipids. By removing lipids, large amounts of amylose and amylopectin solubilized [4] and amylose did not remain in starch granule (Table 2), just because gel was hardly formed and remained unchanged after storage. After 5 days of storage, hardness increases are also shown and ratios of the change by storing are opposite to those of whole starch gels by the presence or absence of lipids. From these results, hardness of rice starch gel is affected by the proportion of amylose and amylopectin. Furthermore, it is interesting that the ratio of the hardness changes by storing shows higher value in water-insoluble fraction of starch. This suggests that amylopectin should make gel hardness high by aging and that the increase of gel hardness is suppressed by the fraction solubilized by defatting which would interact with amylopectin.

3.3 Effects of water-soluble amylose and amylopectin on hardness of rice starch gel

The above results suggest that proportion of amylose and amylopectin affects gel hardness (Table 2 and 3). Then, mixture of normal and waxy rice starches in the presence or absence of lipids was supplied to measure gel hardness.

Table 4 shows the amount of water-soluble carbohydrates in the supernatants from the mixture of normal and waxy rice starches. For nondefatted starch, with an increasing nondefatted waxy starch in proportion the amount of water-soluble carbohydrate increases, and above 80 % of nondefatted waxy

Tab. 4. Effect of lipids on water-solubility in the gelatinization of mixed normal and waxy rice starches.

Proportion (%)		Water-soluble carbohydrate (%)		
Normal	Waxy	Total[a]	Amylose[b]	Amylopectin[b]
Nondefatted				
100	0	10.4 ± 0.3[c] (100)[d]	9.2 (88)[d]	1.2 (12)[d]
80	20	11.6 ± 0.7 (100)	7.4 (64)	4.2 (36)
60	40	13.5 ± 0.9 (100)	6.5 (48)	7.0 (52)
40	60	18.5 ± 0.5 (100)	6.7 (36)	11.8 (64)
20	80	28.3 ± 0.6 (100)	6.3 (22)	22.0 (78)
0	100	28.4 ± 0.3 (100)	1.8 (6)	26.6 (94)
Defatted				
100	0	31.9 ± 0.5 (100)	20.3 (64)	11.6 (36)
80	20	32.0 ± 0.2 (100)	19.3 (60)	12.7 (40)
60	40	29.5 ± 0.5 (100)	15.1 (51)	14.4 (49)
40	60	28.6 ± 0.6 (100)	12.6 (44)	16.0 (56)
20	80	28.4 ± 0.6 (100)	6.8 (24)	21.6 (76)
0	100	28.7 ± 0.4 (100)	2.3 (8)	26.4 (92)

[a, b] The same as shown in Table 2.
[c] Mean ± SD (four measurements).
[d] A percentage of amylose and amylopectin out of the total amount of 100 %.

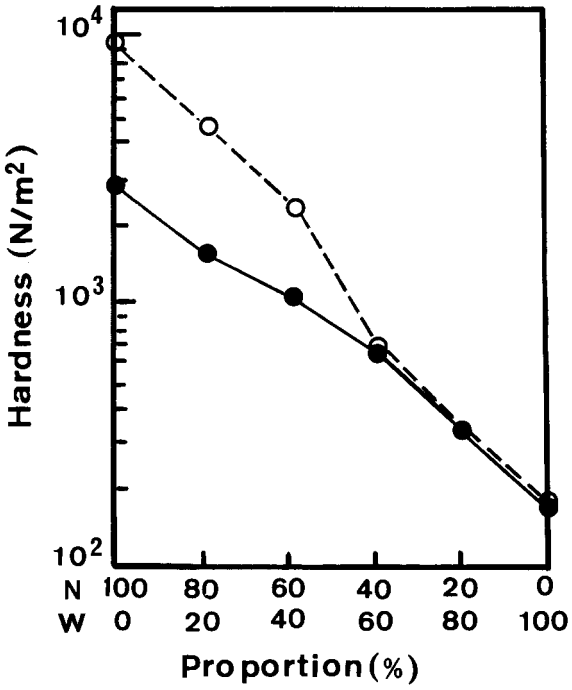

Fig. 2. Effect of lipids on the hardness of the mixed normal and waxy rice starch gels.
Nondefatted (native) starch (–●–); defatted starch (–○–). N, normal; W, waxy.

starch in the mixture, the water-soluble amount comes to be unchanged. For defatted starch, with an increasing defatted waxy starch in proportion the water-soluble amount decreases a little, and above 60 % of defatted waxy starch in the mixture, the water-soluble amount comes to be unchanged. And for both nondefatted and defatted mixed starches, the amounts of water-soluble amylose decrease and the amounts of water-soluble amylopectin increase with an increasing waxy rice starch. Moreover, above 80 % of waxy rice starch for both nondefatted and for defatted starch mixtures, lipids hardly affect the amount of water-soluble carbohydrates.

Fig. 2 shows hardness of mixed starch gel. Here, gel was not formed for the nondefatted mixture of more than 40 % of waxy starch (ratio of water-soluble amylose to amylopectin was 48 to 52) and for the defatted mixture of more than 60 % of waxy starch (ratio of water-soluble amylose to amylopectin was 44 to 56) (Table 4). When the amount of water-soluble amylopectin occupies over a half of water-soluble carbohydrate, gel cannot be formed. So, the water-insoluble fraction of starch which had a very large amount of amylopectin did not naturally form gel (Table 3).

Gel hardness for 100 % of normal rice starch increased by defatting. With an increasing waxy starch, gel hardness decreased in the presence or absence of lipids, and in the mixtures of less than 40 % of normal and more than 60 % of waxy rice starches, it was not affected by lipids.

These results indicated that for the mixed starch consisting of a large amount of amylopectin and a small amount of amylose, the amount of water-soluble carbohydrate in the gelatinization and the gel hardness in the retrogradation was not affected by lipids.

3.4 Interaction among lipids, amylose and amylopectin

It is well known that amylose forms complexes with lipids, whereas amylopectin shows little evidence of interaction with lipids, although some kinds of hydrophilic surfactants are postulated to form weak complexes with amylopectin [26, 27]. From this point of view, our previous study interestingly showed that the water-soluble amount of amylopectin in normal starch paste was much enhanced by defatting and the amount of water-soluble amylopectin in nondefatted starch paste increased early in the aging process, as the amount of soluble amylose increased in both cases [4].

The distribution profiles of the chain length of amylopectins from normal and waxy rice starches were similar [28]. To further investigate an interaction among lipids, amylose and amylopectin, formations of helical complexes of amylose and amylopectin with palmitic acid were evaluated by measuring water-insolubility and precipitation the 100 % of which are defined as the decrease in the amount of water-soluble carbohydrates (90.3 %) and as the amount of precipitate (87.4 %), respectively, both by adding palmitic acid to amylose.

Fig. 3. shows water-insolubility and precipitation of the mixture of amylose and amylopectin from the normal and waxy rice starches. With an increase of amylopectin, water-insolubility and precipitation decrease in value. Both results show the formation of complex of amylopectin with palmitic acid. Below 40 % of amylopectin, the complex formation is above the theoretical value, and above 60 % of amylopectin, it is below the theoretical one. These results seem to indicate that lipids have much effect on complex formation of amylopectin with palmitic acid in the presence of amylose.

These facts show that lipids can indirectly affect the behavior of amylopectin through complex formation with amylose, which may be associated with amylopectin with a starch granule as postulated by *Blanshard* [29]. *Jane* et al. [30] reported that using cross-linking reagents, amylose was cross-linked to amylopectin in granular starch. Furthermore, *Kasemsuwan* and *Jane* [31] reported by the GPC analysis and the phosphorus-31 NMR spectroscopy, that amylose molecules were randomly interspersed among amylopectin; amylose must be located in close proximity with amylopectin for them to be cross-linked. The other studies also indicated the interaction among amylopectin, amylose and lipids [32–35].

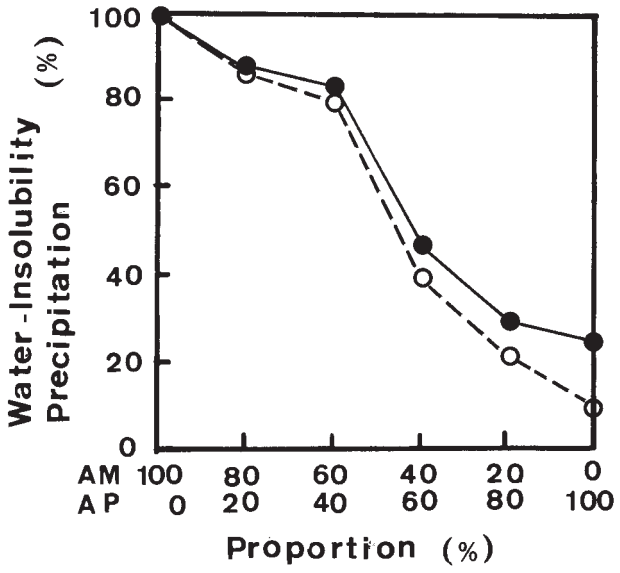

Fig. 3. Water-insolubility (–●–) and precipitation (–○–) of the mixture of amylose and amylopectin from rice starch. AM, amylose; AP, amylopectin.

Bibliography

[1] *Schoch, T._J.:*Baker's Digest **39** (1965), 48.
[2] *Rogers, D. E., K. J. Zeleznak, C. S. Lai,* and *R. C. Hoseney:* Cereal Chem. **65** (1988), 398.
[3] *Kitamura, S., M. Asada, T. Kuge,* and *K. Esaki* (in Japanese): New Food Industry **32-9** (1990), 71.
[4] *Hibi, Y., S. Kitamura,* and *T. Kuge:* Cereal Chem. **67** (1990), 7.
[5] *Miles, M. J., V. J. Morris, P. D. Orford,* and *S. G. Ring:* Carbohydr. Res. **135** (1985), 271.
[6] *Hibi, Y.:* Starch/Stärke **46** (1994), 44.
[7] *Bhattacharya, K. R., C. M. Sowbhagya,* and *Y. M. Indudhara Swamy:* J. Food Sci. **37** (1972), 733.
[8] *Bhattacharya, K. R., C. M. Sowbhagya,* and *Y. M. Indudhara Swamy:* J. Sci. Food Agric. **29** (1978), 359.
[9] *Bhattacharya, K. R.,* and *C. M. Sowbhagya:* J. Food Sci. **44** (1979), 797.
[10] *Bhattacharya, K. R.,* and *C. M. Sowbhagya:* J. Sci. Food Agric. **31** (1980), 615.
[11] *Bhattacharya, K. R., C. M. Sowbhagya,* and *Y. M. Indudhara Swamy:* J. Food Sci. **47** (1982), 564.
[12] *Sowbhagya, C. M., B. S. Ramesh,* and *K. R. Bhattacharya:* J. Cereal Sci. **5** (1987), 287.
[13] *Gray, V. M.,* and *T. J. Schoch:* Starch/Stärke **14** (1962), 239.
[14] *Ohashi, K., G. Goshima, H. Kusuda,* and *H. Tsuge:* Starch/Stärke **32** (1980), 54.
[15] *Morad, M. M.,* and *B. L. D'Appolonia:* Cereal Chem. **57** (1980), 141.
[16] *Eliasson, A.-C.:* Starch/Stärke **37** (1985), 411.
[17] *Hoover, R.,* and *D. Hadziyev:* Starch/Stärke **33** (1981), 290.
[18] *Nakazawa, F., S. Noguchi, J. Takahashi,* and *M. Takada:* Agric. Biol. Chem. **48** (1984), 201.
[19] *Mano, Y.,* and *Y. Fujino* (in Japanese): J. Jpn. Soc. Starch Sci. **22** (1975), 1.
[20] *Mano, Y., M. Ohnishi,* and *S. Ito* (in Japanese): J. Jpn. Soc. Starch Sci. **35** (1988), 49.
[21] *Kuge, T.,* and *K. Tenichi:* Agr. Biol. Chem. **32** (1968), 1232.
[22] *Hodge, J. E.,* and *B. T. Hofreiter:* in: Methods in Carbohydrate Chemistry. I. Eds. R. S. Whistler, and M. L. Wholfrom. Academic Press, London 1962, pp. 388.
[23] *Kitamura, S., H. Yunokawa, S. Mitsuie,* and *T. Kuge:* Polym. J. **14** (1982), 93.
[24] *Inaba, K., Y. Hatanaka, O. Kageyama, Y. Matsumura,* and *T. Mori* (in Japanese): J. Jpn. Soc. Food Sci. and Techn. **36** (1989), 884.
[25] *Ott, M.,* and *E. E. Hester:* Cereal Chem. **42** (1965), 476.
[26] *Evans, I. D.:* Starch/Stärke **38** (1986), 227.
[27] *Eliasson, A.-C., H. Finstad,* and *G. Ljunger:* Starch/Stärke **40** (1988), 95.
[28] *Hibi, Y.* (in Japanese): New Food Industry **32-5** (1990), 63.
[29] *Blanshard, J. M. V.:* in: Starch: Properties and Potential. Ed. T. Galliard. John Wiley & Sons, Chichester 1987, pp. 16.
[30] *Jane, J., A. Xu, M. Radosavljevic,* and *P. A. Seib:* Cereal Chem. **69** (1992), 405.
[31] *Kasemsuwan, T.,* and *J. Jane:* Cereal Chem. **71** (1994), 282.
[32] *Tester, R. F.,* and *W. R. Morrison:* Cereal Chem. **67** (1990), 551.
[33] *Tester, R. F.,* and *W. R. Morrison:* Cereal Chem. **67** (1990), 558.
[34] *Tester, R. F.,* and *W. R. Morrison:* Cereal Chem. **69** (1992), 654.
[35] *Morrison, W. R., R. F. Tester, C. Snape, R. Law,* and *M. J. Gidley:* Cereal Chem. **70** (1993), 385.

Address of author: Dr. *Yoshiko Hibi*, Course of Food and Nutrition, Department of Life Style Studies, School of Human Cultures, The University of Shiga Prefecture, 2500 Hassaka-cho, Hikone 522-8533, Japan.

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Ageing of Starch Based Systems as Observed with FT-IR and Solid State NMR Spectroscopy

Angela L. M. Smits, Frank C. Ruhnau, Johannes F. G. Vliegenthart, Utrecht and Jeroen J. G. van Soest, Wageningen (The Netherlands)

The retrogradation and physical ageing of model starch systems with respect to their glass transition temperatures T_g have been investigated by Fourier transform infrared spectroscopy and solid state NMR spectroscopy. Diffuse reflectance Fourier transform infrared (DRIFT) spectra demonstrate the commencing retrogradation of starch materials stored above their T_g by changes in peak lineshapes and intensities in the characteristic area between 995 cm^{-1} and 1020 cm^{-1}. Solid state NMR proton relaxation times in the rotating frame (proton $T_{1\rho}$) show a characteristic course in relation to the storage conditions (time, humidity), for which a distinction is made between physical ageing which occurs below the T_g, and recrystallisation (retrogradation) which takes place above T_g. The proton $T_{1\rho}$'s of materials stored below T_g increase asymptotically in time due to physical ageing, whereas the proton $T_{1\rho}$'s of materials stored above T_g increase until a moisture content is reached that rises them above T_g, decrease due to further water absorption and then increase due to recrystallisation (retrogradation).

Introduction

Starch is one of the main energy providers in the human diet and it is being used for many years as a natural food-thickener [1]. In the food industry plasticisers like water and sugars are used to improve the food quality and to delay the loss of moisture and the staling of food products, which limit the shelf-life of bakery products.

Lately there is much interest in biodegradable plastics to replace synthetic short-lifecycle products. Starch, for example, is a cheap biopolymer that is totally biodegradable forming carbon dioxide and water. Granular starch is mixed with suitable plasticisers to enable melting below the decomposition temperature, resulting in thermoplastic starch (TPS) [2, 3].

The time dependent behaviour of starch based materials during and after processing is of great importance in the food industry and for the development of bioplastics. Especially rheological and physico-chemical changes during storage (ageing) are important. Because the predominantly amor-