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DSC and rheological studies of the effects of sucrose on the gelatinization and retrogradation of acorn starch

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Abstract

The effects of sucrose on the gelatinization and retrogradation of acorn starch were studied by differential scanning calorimetry, compression and longitudinal oscillation measurements of cylindrically molded gels. All these measurements showed that sucrose retarded the retrogradation of acorn starch effectively. Regelatinization enthalpy of acorn starch dispersion stored for 14 days depended strongly on the concentration of added sucrose but not so much for the dispersion stored for one day, suggesting that the interaction between sucrose and amylose is less important than the interaction between sucrose and amylopectin. © 1998 Elsevier Science B.V.

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1. Introduction

Starch has been widely used in food, textile, paper, and other industries because of its unique properties and low price [1]. Starch is not a uniform raw material with clearly defined properties, but a multi-component system consisting of linear amylose with α-1,4 linked glucopyranoside units, and amylopectin with both, α-1,4 and α-1,6 linked units giving a branched structure. Physico-chemical properties of search depend not only on the molecular structure but also on the morphology of the starch species.

Acorn starch is composed of a mixture of amylose and amylopectin and minor impurities, such as crude fat, proteins, fibers, minerals, and tannin [2]. Acorns have been consumed in the form of bread, cake and confectionary in Europe and commonly used for making 'mook' in Korea.

When starch is heated in the presence of sufficient amounts of water, starch granules are swollen and the ordered structure is changed into a disordered one, and this phenomenon is called gelatinization. Retrogradation of starch is a term used for the change that occurs in gelatinized starch for an initially amorphous or disordered state to a more ordered or crystalline state and the tendency of starch pastes to thicken and to form stiff gels. The development of turbidity and opacity, syneresis of water from the paste occur during the retrogradation. Miles et al. [3] have interpreted that retrogradation takes place in two crystallization steps: the rigidity and crystallinity of starch gels develop by amylose gelation in the initial stage and this is fol-

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lowed by the slow development of crystallinity of amylopectin. The changes of physico-chemical properties in gelatinized starch have been studied by means of differential scanning calorimetry (DSC) [4–10], mechanical compression test [11–13], and dynamic mechanical spectroscopy [14–16].

DSC analysis has often been applied to measuring the rate and extent of starch recrystallization on aging [7,17]. The anti-staling role of native granular lipids or surfactants in starch gels or dough systems has been confirmed by DSC measurement [18]. Retrogradation rate is affected by the ratio of amylose and amylopectin, molecular size, temperature, pH, lipids, hydrocolloids, sugar and botanical sources [1].

Sugars are known to function as anti-staling ingredients [19]. Many investigators have studied the effect of sugars on gelatinization [20–23]. To investigate the effects of sucrose on the retrogradation of acorn starch, effects of sucrose concentration on the rheological and thermal properties of acorn starch gels have been examined in the present work.

Though a few studies acorn starch gel have been done [2,24–26], a comparative study on the rheological and thermal properties have not yet been performed.

2. Materials and methods

2.1. Materials

Acorn powder was purchased in the cultured place Keyngsangnamdo, Korea and purified according to the method of Schoch et al. [27]. Sucrose of reagent grade was purchased from Wako Pure Chemical Ind. Ltd. (Osaka) and used without further purification. Moisture content of the purified starch was determined as 9.35% by the oven-drying method. The amylose content in acorn starch (AS) was determined by iodimetry [28] at 28%.

2.2. Preparation of gels

The gels of acorn starch with, or without, sucrose were prepared as described by Yoshimura et al. [29]. Forty-five grams of AS powders were dispersed in 300 ml of distilled water containing 0.02% NaN_3 as preservative. The dispersion was stirred with a motorized stirrer (Heidon 3000 H, Shintoh, Tokyo, Japan) at 300 rpm for 2 h at room temperature. Then, the dispersion was heated in a silicone oil bath to 95°C and then kept at 95–98°C for 30 min. The dispersion was kept stirring at 400 rpm during heating. In order to supplement evaporating water during heating, boiling distilled water was added. The hot dispersion was poured into cylindrical Teflon molds of 20 mm diameter and 20 or 30 mm height and cooled at room temperature for 1 h. Thereafter, gels formed were stored at 5°C and immersed in silicone oil to prevent moisture loss.

2.3. Differential scanning calorimetry

The extent of gelatinization and retrogradation was measured by a differential scanning calorimeter PTC10D (Rigaku Denki, Tokyo, Japan). The powdered mixtures of AS with, and without, sucrose and water were directly weighed in a silver pan of 70 μl and the pan was hermetically sealed. Subsequently, the sample pan was reweighed and allowed to stand overnight at room temperature. A pan containing an equal amount of water was used as a reference. The temperature was raised from 25 to 30°C at the heating rate of 1.0°C/min. After the first heating run, the pan was quenched immediately in liquid nitrogen from 130°C to 5°C and stored at 5°C for various storage times. In the second run heating, the temperature was raised from 5° to 130°C at the same heating rate. Enthalpy and onset temperature (T_0), peak temperature (T_p) and conclusion temperature (T_c) were determined. Biphenyl was used for calibrating the temperature and enthalpy.

2.4. Compression test of cylindrical gels

Compression test of a gel at different storage times was carried out by uniaxial compression between two parallel plates. Experiments were conducted by a creep meter (Rheoner RE-3305, Yamaden, Tokyo, Japan) equipped with a 2-kg load cell and the cross-head speed of 30 mm/min. These experiments were repeated more than 12 times and the mean value and standard deviation were determined. The Young's modulus was determined from the initial slope of stress–strain curves.

2.5. Dynamic mechanical measurement

The dynamic mechanical properties of the gels were examined as a function of storage time and temperature using a rheolograph gel (Toyo Seiki Seisakusho, Tokyo, Japan) at a frequency of 3 Hz and an amplitude of 100 μm. The temperature was controlled by a silicone oil bath at each measurement temperature within 0.1°C. A cylindrical gel is subjected to sinusoidal longitudinal oscillations. The stress is divided into the component in phase with the applied strain and the component with leading phase $\pi/2$ to the applied strain. These values are proportional to storage Young's modulus E', and loss Young's modulus E'', respectively, and are indicated in digital display [30].

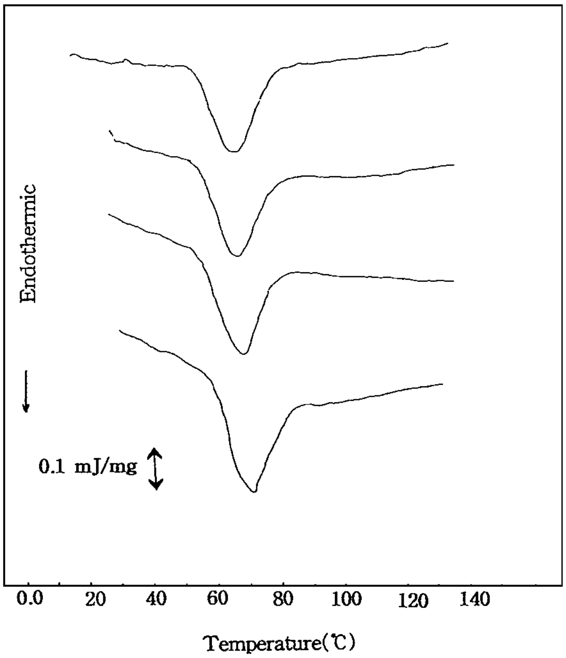

Fig. 1. Heating DSC curves of 15 wt% acorn starch dispersions in the presence of different sucrose concentrations. The concentrations of sucrose are 0, 5, 10 and 15 wt% from top to bottom. Heating rate: 1°C/min.

3. Results and discussion

3.1. Differential scanning calorimetry

The heating DSC curves for gels of AS with, and without, sucrose are shown in Fig. 1. A single endothermic peak was observed, accompanying gelatinization at high water content (more than 60% w/w), as has been observed for many starches [4].

As shown in Fig. 1, the gelatinization peak shifted to higher temperatures with increasing sucrose concentration. Table 1 shows the onset temperature T_0, peak temperature T_p, and conclusion temperature T_c of the endothermic peak, and the endothermic enthalpy ΔH_1 of gelatinization for gels of AS with, and without, sucrose. T_0, T_p and T_c shifted to higher temperatures, and ΔH_1 increased with increasing sucrose concentration. These results are in agreement with those reported in the literature [10,22]. Sucrose may change the structure of water as a solvent, and immobilizes water molecules. It is well known that the conformation of glucose well matches the tridymite structure in water [31,32], and that the equatorial hydroxyl groups in a sugar molecule may be effectively substituted for a water molecule, and hence the hydration of sugar hydroxyl groups has a stereospecific nature. Then, a sugar molecule with more equatorial hydroxyl groups has a stronger stabilizing effect on the water structure [33]. The swelling of starch granules in sugar solution may occur at higher temperatures and requires much more energy in comparison with aqueous dispersion of starch without sucrose. This is consistent with the experimental findings for sweet-potato starch that the order of the effectiveness of various sugars to shift the gelatinization temperatures to higher values and to

Table 1
The temperature and enthalpy of gelatinization for A.S and A.S plus sucrose gels

Sucrose concentration (% w/w)	T_o	T_p	T_c	ΔH(mJ/mg)
0	55(35)	64.57(53.5)	74.3(64.57)	9.18 0.19
5	56.25(34.5)	66.38(52)	75.5(64)	9.76 0.025
10	58.43(34)	67.8(51.5)	76.5(63.5)	9.93 0.11
15	59(33.5)	69.38(49.5)	78.4(63)	10.26 0.08

increase the gelatinization enthalpy: sucrose was the most effective and fructose the least effective, and glucose was the intermediate [10]. This order agrees with the dynamic hydration number of these sugars n_{DHN}=25.2 for sucrose, 18.6 for glucose and 16.5 for fructose [33,34]. On the other hand, the reason for the observed increase in endothermic enthalpy and the shift of the peak temperature to higher values with increasing concentration of added sucrose in sweet-potato starch was attributed to the stabilization of the ordered region of starch on the basis of zipper model approach [10,35]. The rotational freedom of segments constituting a molecular zipper, i.e. molecular chains in a fringed micellar model for starch, decreased and the number of parallel links which forms a single zipper decreased and the number of zippers increased with increasing concentration of added sugars [10]. It is difficult to estimate quantitatively, at present, to which extent the change of water structure and the direct interaction between sugars and starch contribute to the shift of gelatinization peak temperature to higher values and the increase in the gelatinization enthalpy; it should be further explored in the future.

Fig. 2 shows the heat required for regelatinization (ΔH_2) for gels of AS, and AS plus sucrose, as a function of sucrose concentration. As shown in Fig. 2, the enthalpy of the second DSC heating run decreased with increasing sucrose concentration and tends to saturate after 14 days for each gel. The retrogradation ratio, estimated by $\Delta H_2/\Delta H_1$ [10], as a function of storage time for each gel is shown in Fig. 3. The retrogradation ratio increased with time, and it was smaller for gels with higher sucrose content than for gels with lower sucrose content. In the short storage time, the effect of sucrose on the retrogradation ratio is not so dependent on sucrose concentration. From Fig. 3, it seems that sugar acts as an anti-staling reagent and, hence, retards the retrogradation.

It has been reported that retrogradation consists of two separable processes [3]. The first stage is governed by the gelation of amylose solubilized during

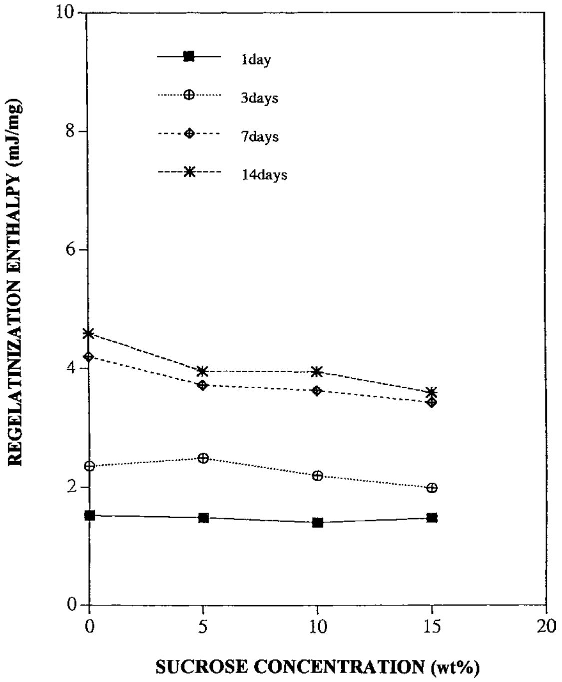

Fig. 2. Regelatinization enthalpy of acorn starch gels with various storage times as a function of concentration of added sucrose.

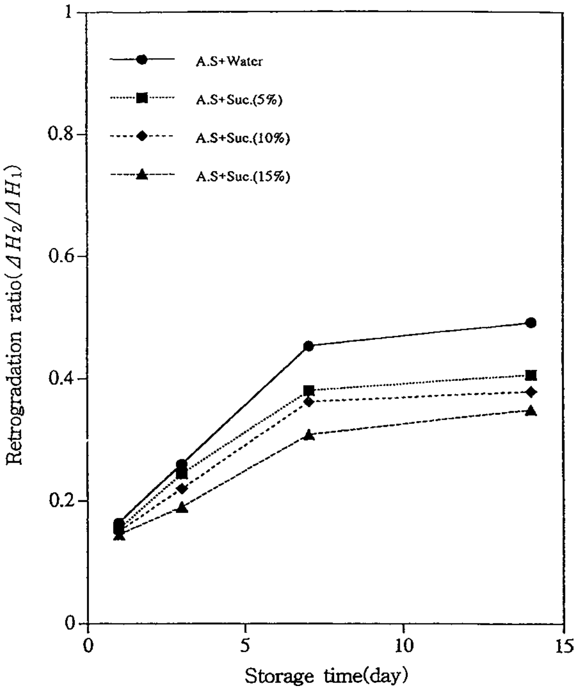

Fig. 3. Retrogradation ratio of 15 wt% acorn starch dispersions with, and without, sucrose as a function of storage time.

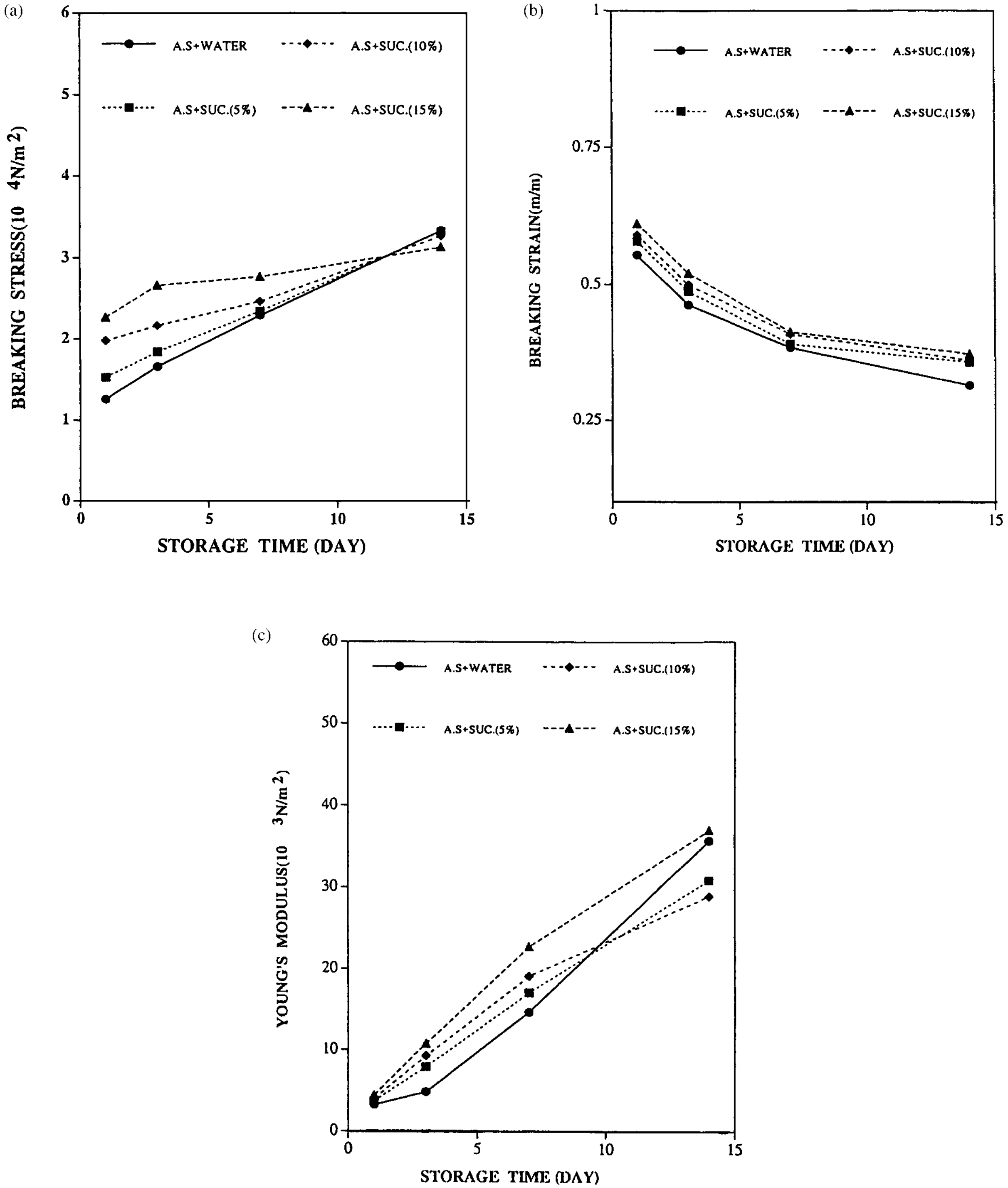

Fig. 4. Breaking stress (a) breaking strain (b) and Young's modulus (c) of 15 wt% acorn starch gel with, and without, sucrose as a function of storage time. Temperature of storage and measurement, 5°C. Compression speed, 30 mm/min.

gelatinization and the second stage is induced by the recrystallization of amylopectin within the gelatinized granules. Since the regelatinization enthalpy shown in Fig. 2 was not so dependent on the concentration of sucrose for samples stored for one day, and was strongly dependent on the concentration of sucrose for samples stored for 14 days, the anti-staling effect of sucrose should be more important for the interaction of sucrose with amylopectin rather than with amylose. This is consistent with experimental findings shown in Fig. 5 for normalized Young's modulus of acorn starch gels with, and without, sucrose: Young's modulus, E, after storage of 14 days was the largest for a gel without sucrose, and E decreased with increasing concentration of added sucrose. It is urgently required to confirm this point by studying the effects of sugars on the retrogradation of starch with different amylose and amylopectin ratios.

3.2. Compression test of gels

The results of compression measurement for gels of AS alone, and AS with sucrose, as a function of storage time are shown in Fig. 4. The average value and standard deviation of breaking stress, breaking strain and Young's modulus as a function of storage time are shown in Table 2. For all the gels, breaking stress (Fig. 4(d)) and Young's modulus (Fig. 4(c)) increased, and the breaking strain (Fig. 4(b)) decreased with storage time. Similar results were reported by Keetels et al. [13] for gels prepared from various types of potato starch and by Yoshimura et al. [29] for corn starch gels.

In the initial stage, the breaking stress and Young's modulus of a gel with sucrose were large than those of gel without sucrose. As was suggested previously [10], the number of zippers and the elastically active network chains increased by the addition of sugars, hence both breaking stress and Young's modulus increased. After seven days, the breaking stress and Young's modulus for a gel containing sucrose increased more slowly with storage time compared to a gel of AS alone. The breaking stress for the gel containing 15% w/w sucrose showed the lowest value after two weeks.

Breaking strain decreased during storage time in all of the gels. As the concentration of sucrose increased, breaking strain tended to larger values, indicating the retrogradation of starch was retarded by sucrose.

3.3. Dynamic mechanical measurement

The storage Young's modulus (E') and loss Young's modulus (E'') of gels of 15 wt% AS alone and 15 wt% AS with sucrose of various concentrations as a function of storage time are shown in Figs. 5 and 6. In Fig. 5, the storage Young's modulus E' as a function of storage time is normalized, i.e. the value of E' is divided by the initial value of E'_e of the value E' after one day storage. In the initial stage, the storage Young's modulus of a gel increased with increasing concentration of added sucrose. This is in good agreement with the experimental results of compression test.

The temperature dependence of the storage Young's modulus (E') and the mechanical-loss tangent, tan δ,

Table 2
Breaking stress, Breaking strain and Young's modulus of gels a function of storage time

Sample	Breaking Stress (10^4N/m^2)				Breaking Strain (m/m)				Young's Modulus (10^3N/m^2)			
	A.S+ Wat	A.S+ S(5)	A.S+ S(10)	A.S+ S(15)	A.S+ Wat	A.S+ S(5)	A.S+ S(10)	A.S+ S(15)	A.S+ Wat	A.S+ S(5)	A.S+ S(10)	A.S+ S(15)
1	1.262	1.529	1.983	2.268	0.554	0.578	0.591	0.611	3.249	3.742	4.036	4.433
	0.128	0.028	0.103	0.142	0.006	0.008	0.009	0.012	0.184	0.204	0.185	0.215
3	1.665	1.844	2.171	2.665	0.463	0.487	0.499	0.520	4.860	7.904	9.265	10.78
	0.119	0.035	0.144	0.187	0.022	0.019	0.009	0.015	0.449	0.08	0.092	0.111
7	2.297	2.348	2.471	2.770	0.384	0.391	0.409	0.413	14.68	17.07	19.09	22.71
	0.034	0.207	0.319	0.403	0.012	0.013	0.015	0.029	0.199	0.112	0.101	0.275
14	3.337	3.324	3.269	3.133	0.384	0.357	0.361	0.372	35.67	30.79	28.87	36.93
	0.063	0.080	0.257	0.094	0.021	0.009	0.016	0.016	0.258	0.301	0.049	0.241

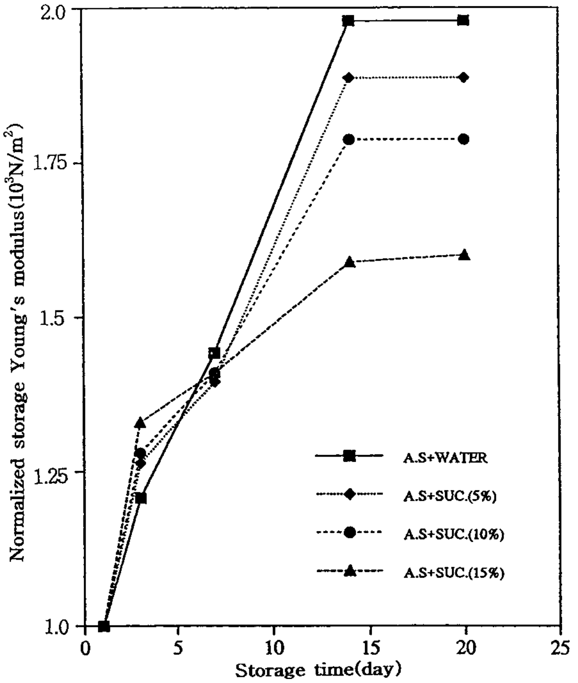

Fig. 5. Normalized storage Young's modulus (3 Hz) of 15 wt% acorn starch gel with, and without, sucrose as a function of storage time. Temperature of storage, 5°C. Temperature of measurement, 15°C.

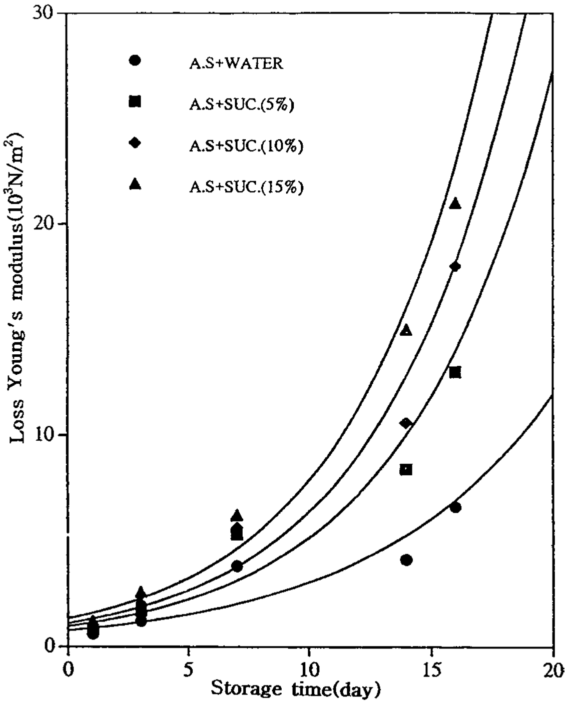

Fig. 6. Loss Young's modulus (3 Hz) of 15 wt% acorn starch gel with, and without, sucrose as a function of storage time. Temperature of storage, 5°C. Temperature of measurement, 15°C.

of gels of AS with, and without, sucrose after one day's storage is shown Fig. 7. At any temperature, E' of gels with higher sucrose content was larger than E'‰ of gels with lower sucrose content. E' decreased monotonically with increasing temperature, which indicates that the network structure of gels was weakened by heating. This is in accordance with fringed micellar model in which the ordered structure in starch gels are made mainly by hydrogen bondings.

Cheer and Lelievre [36] reported that the effect of sucrose at concentrations of less than ca. 20 wt% is to increase the apparent viscosity, yield stress, dynamic viscosity and dynamic rigidity for wheat starch paste. It was suggested that sucrose caused the dispersed gel particles in pastes to change volume, and that it was one of the factors responsible for the observed effects of sucrose on retrogradation behavior. Germani [37] reported that the elastic modulus of corn starch gel with sucrose was larger than that of corn starch alone in the initial stage. But after five days, the elastic modulus of a gel of corn starch alone was found to be larger than that of a gel containing sucrose. Schenz [38] reported that sucrose acts as an anti-plasticizer, since its molecular weight is greater than that of the primary plasticizer of starch, namely water. He suggested that adding sucrose increases the net molecular weight of the plasticizer solvent, and increases the glass transition temperature T_g and, subsequently the gelatimization temperature T_{gel}.

It is suggested that sucrose should interact with the starch component (amylose or amylopectin, or both) or interface in some way with the association of molecules or promote the formation of network structure. In the longer storage time, breaking stress, Young's modulus, storage Young's modulus and reheating enthalpy increased with storage time but decreased with increasing sucrose concentration. Breaking strain decreased with storage time, and it was impeded by sucrose. Long-term increase in the modulus of starch gels was linked to a reversible crystallization, involving amylopectin within the granules on storage [3].

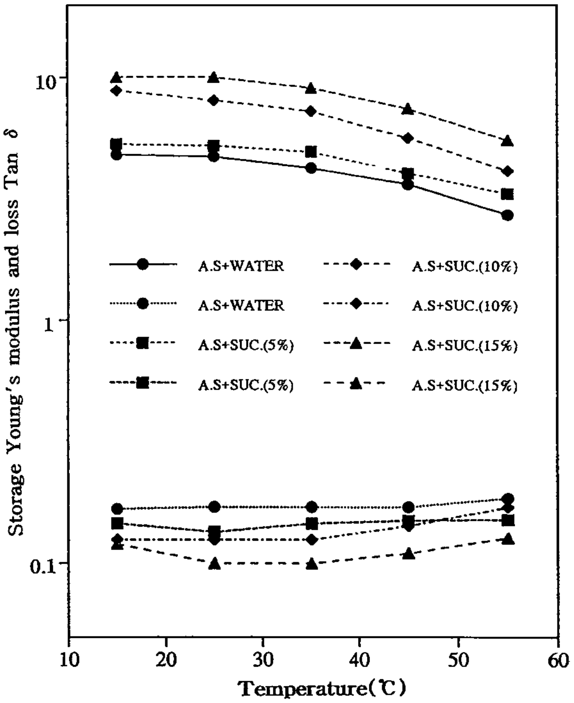

Fig. 7. Temperature dependence of storage Young's modulus and loss tan δ (3 Hz) of 15 wt% acorn starch gel stored for one day at 5°C with, and without, sucrose.

There are many papers reporting that the development of gel stiffness is closely related to the association of amylopectin chains [16,18,39,40]. It is suggested that, in the longer storage time, sucrose prevents the rearrangement of molecular chains which tend to form a more ordered structure or a crystalline structure, i.e. sucrose acts as an anti-staling reagent, and hence retards the retrogradation.

References

[1] H.F. Zobel, A.M. Stephen, in: A.M. Stephen (Ed.), Food Polysaccharides and their Applications, Marcel Dekker, New York, 1995, p. 19.
[2] D.H. Chung, T.J. Yu, B.G. Choi, Korean J. Agric. Chem. Soc. 18 (1975) 102.
[3] M.J. Miles, V.J. Morris, P.D. Orford, S.G. Ring, Carbohydr. Res. 135 (1985) 271.
[4] C.G. Biliaderis, in: V.R. Harwalkar, C.-Y. Ma (Eds.), Thermal Analysis of Foods, Elsevier Applied Science, London, 1990, p. 168.
[5] J.W. Donovan, Biopolymers 18 (1979) 263.
[6] T. Shiotsubo, K. Takahashi, Agric. Biol. Chem. 48 (1984) 9.
[7] T.P. Jankowski, C.K. Rha, Starch 38 (1986) 6.
[8] H.F. Zobel, Starch 40 (1988) 1.
[9] Ph. Roulet, W.M. MacInnes, P. Wursch, R.M. Sanchez, A. Raemy, Food Hydrocoll. 2 (1988) 381.
[10] K. Kohyama, K. Nishinari, J. Agric. Food Chem. 39 (1991) 1406.
[11] S.K. Kim, B.L. Dappolonia, Cereal Chem. 54 (1977) 150.
[12] K. Katsuta, A. Nishimura, M. Miura, Food Hydrocoll. 6 (1992) 399.
[13] C.J.A.M. Keetels, T. Van Vliet, P. Walstra, Food Hydrocoll. 10 (1996) 355.
[14] R.B.K. Wong, J. Lelievre, Starch 34 (1982) 231.
[15] M. Mizukishi, Cereal Chem. 62 (1985) 247.
[16] S.G. Ring, P. Colonna, K.J. I'anson, M.T. Kalichevsky, M.J. Miles, V.J. Morris, P.D. Orford, Carbohydr. Res. 162 (1987) 277.
[17] K.J. Zeleznak, R.C. Hoseney, Cereal Chem. 63 (1986) 407.
[18] M. Gudmundsson, A.C. Eliasson, Carbohydr. Polym. 13 (1990) 295.
[19] L. Slade, H. Levine, in: J.E. Kinsella (Ed.), Advances in Food and Nutrition Research, vol. 38, Academic Press, 1994.
[20] M.M. Bean, W.T. Yamazaki, D.H. Donelson, Cereal Chem. 55 (1978) 945.
[21] H.L. Savage, E.M. Osman, Cereal Chem. 57 (1980) 49.
[22] R.D. Spies, R.C. Hoseney, Cereal Chem. 59 (1982) 128.
[23] A.M. Abboud, R.C. Hoseney, Cereal Chem. 61 (1984) 34.
[24] S.J. Koo, J. Korean Home Eco. 22 (1984) 99.
[25] Y.A. Kim, H. Rhee, Korean J. Food Sci. Technol. 17 (1985) 469.
[26] S.J. Koo, J.O. Chang, N. Nakahama, M. Kobayashi, J. Korean Home Eco. 23 (1985) 33.
[27] T.H. Schoch, E.J. Wilson, C.S. Hudson, J. Am. Chem. Soc. 65 (1943) 1380.
[28] B. Carroll, H.C. Cheung, Method in Carbohydrate Chemistry, Academic Press, New York, 1964, p. 170.
[29] M. Yoshimura, T. Takaya, K. Nishinari, J. Agric. Food. Chem. 44 (1996) 2970.
[30] K. Nishinari, H. Horiuchi, K. Ishida, K. Ikeda, M. Date, E. Fukada, Nippon Shokuhin Kogyo Gakkaishi 27 (1980) 227.
[31] H. Uedaira, M. Ikura, H. Uedaira, Bull. Chem. Soc. Jpn. 62 (1989) 1.
[32] M.A. Kabayama, D. Patterson, Can. J. Chem. 36 (1958) 563.
[33] H. Uedaira, in: K. Nishinari, T. Yano (Eds.), Science of Food Hydrocolloids, Asakura Shoten, 1990, p. 42.
[34] H. Uedaira, H. Uedaira, J. Solution Chem. 14 (1985) 27.
[35] K. Nishinari, S. Koide, P.A. Williams, G.O. Phillips, J. Phys. (France) 51 (1990) 1759.
[36] R.L. Cheer, J. Lelievre, J. Appl. Polym. Sci. 28 (1983) 1829.
[37] R. Germani, C.F. Ciacco, D.B. Rodriguez, Starch 35 (1983) 377.
[38] T.W. Schenz, Food Hydrocoll. 9 (1995) 307.
[39] M.T. Kalichevsky, P.D. Orford, S.G. Ring, Carbohydr. Res. 198 (1990) 49.
[40] M.T. Kalichevsky, E.M. Jaroszkiewicz, S.A. Blett, J.M.V. Blanshard, P.J. Lillford, Carbohydr. Polym. 18 (1992) 77.