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Changes with retrogradation of mechanical and textural properties of gels from various starches

Hisaji Inaba, Yoshio Hatanaka, Takashi Adachi,

Central Laboratory, Myojo Food, Co., Ltd., Musashino, Tokyo 180, Japan

Yasuki Matsumura & Tomohiko Mori

Research Institute for Food Science, Kyoto University, Uji, Kyoto 611, Japan

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Gels were prepared from various starch species at three different concentrations for each starch species. The gels were stored at 5°C for 1 to 30 days, and characterized in terms of mechanical parameters measured by a compression–decompression test. Compression work and rupture force increased gradually with storage period. Resiliency and compressibility increased and decreased, respectively, most significantly in the first 5 to 10 days. Changes in mechanical properties of the gels during storage were different among starch species. Changes in textural properties of the gels during storage were evaluated using three-dimensional representation of the gels through factor analysis of instrumental data and calculation of factor scores. The gels were also examined for degree of gelatinization using an enzymatic method. From a regression analysis of those data, the relationship of the change in degree of gelatinization to change in mechanical properties was observed. Resiliency was found to be the most correlative property.

INTRODUCTION

Gelatinized starch returns to an insoluble or aggregated form over a period of time. This phenomenon, called retrogradation, was defined as the changes which occur in a starch paste or gel on ageing (Collison, 1968). A variety of methods have been designed to estimate the degree of starch retrogradation.

Enzymic hydrolysis of starch has been developed to determine the degree of gelatinization and retrogradation of starch (Shetty *et al.*, 1974; Kainuma *et al.*, 1981; Matsunaga & Kainuma, 1986; Tsuge *et al.*, 1990). This technique has been extensively used in studies of starch retrogradation, although there are a number of techniques in the literature that differ in the source of enzyme used.

Another technique, differential thermal analysis, or differential scanning calorimetry, has also been used to estimate gelatinization and retrogradation (Axford & Colwell, 1967; McIver *et al.*, 1968; Nakazawa *et al.*, 1984; Jankowski & Rha, 1986; Zeleznzak & Hoseney, 1986; Roulet *et al.*, 1987, 1988). This calorimetric procedure estimates the changes of hydrogen bonding between hydroxyl groups of adjacent starch molecules and between water and starch molecules that occurs in gelatinization or retrogradation.

X-ray diffractometry has revealed the disappearance and partial recovery of crystalline structure in gelatinized and retrograded starch, respectively, thereby offering a method of assessing the degree of gelatinization and retrogadation in terms of the diffraction pattern (Orford *et al.*, 1987; Roulet *et al.*, 1987, 1988; Hibi *et al.*, 1990; Cairns *et al.*, 1991).

In addition, recently, the movement of starch molecule chains has been analysed by ^{13}C nuclear magnetic resonance (NMR) spectra, and it has been shown that this movement varies with the degree of gelatinization or retrogradation (Kainosho & Ajisaka, 1978; Inaba *et al.*, 1988).

Spectroscopic analyses, rapid-scanning Raman spectroscopy (Bulkin *et al.*, 1987; Winter & Kwak, 1987) and Fourier-transform infrared spectroscopy (Wilson *et al.*, 1987; Wilson & Belton, 1988), have also been proposed as useful methods for evaluating starch retrogradation.

In the case of starch concentrations high enough to form a gel, the change of gel hardness has been examined to estimate the degree of retrogradation (Kim & D'Appolonia, 1977; Ciacco & Fernandes, 1979; Germani *et al.*, 1983; Krüsi & Neukom, 1984; Jankowski & Rha, 1986; Orford *et al.*, 1987; Roulet *et al.*, 1987). The hardening of gel is the outstanding change which occurs in the starch gel on ageing and may involve the changes of various mechanical properties other than the hardness. Recently, a technique to evaluate the physical and textural properties of soy protein gels by measuring mechanical parameters with a compression–decompression tester was reported (Kang *et al.*, 1991). In this paper, we discuss our attempts to evaluate in detail the changes of the starch gel property with time by means of the above technique. Starch gels were measured for the mechanical parameters which relate to hardness, toughness, fracturability and elasticity. The relationship between the changes of physical and textural properties of the gels and the degree of gelatinization or retrogradation by means of the enzymic method has also been examined.

EXPERIMENTAL

Starches

Potato (PO), corn (CO) and wheat (WH) starches were purchased from Wako Pure Chemical Industries, Ltd. (Japan). Tapioca (TA) starch, made in Thailand, was donated by Ajinomoto, Co., Ltd. (Japan). Chemical compositions (moisture, ash, protein and lipids) of starches and the content of amylose from amperometric titration to determine the iodine-binding capacity (Larson *et al.*, 1953) are shown in Table 1.

Preparation and retrogradation of gels

Starch gels in the concentrations of 7–25% (w/v) were prepared according to the following procedure designed to prevent the precipitation of starches. Starch suspensions of 3% (for corn) or 2% (for others) (w/v) were heated at 100°C with stirring (20–30 strokes/min) for 10 min and cooled to ambient temperature, then the starches were added to each fixed concentration as indicated and then suspended well. The suspensions were heated at 100°C for 30 min without stirring and poured into a gap of 2 mm between two glass plates. After cooling to ambient temperature, the plates were allowed to stand for 24 h at either 5 or 20°C to set the gel. Retrogradation progressed by storage of the gels at 5°C.

Table 1. Chemical composition and amylose content of starches

Source of starch[a]	Moisture (%)	Ash (%)	Protein (%)	Lipids (%)	Amylose (%)
PO	16·0	0·23	0·01	0·67	19·3
TA	12·3	0·22	0·14	0·78	17·2
CO	13·6	0·07	0·28	1·06	21·0
WH	13·9	0·21	0·39	2·36	19·1

[a]PO, potato; TA, tapioca; CO, corn; WH, wheat.

Measurement of the mechanical properties of the gels

A uniaxial compression–decompression test was carried out at 20°C using a KES-FB3 Compression Tester (Kato Tech Co. Ltd., Japan) equipped with cylindrical plunger of 0·5-cm^2 cross-section. The sheet of gels were removed from the glass plates and cut to a square with a side of 2 cm. The plunger was moved at 1·2 mm/min. The measurement was carried out by compressing the sample until rupture and then immediately reversing the direction to move upwards at the same speed. This series of tests gave a force–deformation curve. The tests were then carried out at different levels of compression up to rupture: i.e. small, medium and large compression levels for which the forces were set at 15, 30 and 60% of rupture force, respectively. From these tests, the parameters of compression work (CW), rupture force (F), resiliency (RS) and compressibility (CM) at four levels of compression were determined according to the method of Kang *et al.* (1991). The measurements were repeated 5–10 times for each gel sample. The data were reproducible to about ±5% on repeated runs.

Determination of the degree of gelatinization of starch

The gelatinized starch paste before gelling and the retrograded starch gels used for the compression–decompression test were dehydrated with ethanol and acetone, and dried. The resulting powder samples were crushed and passed through a 100-mesh sieve. They were then subjected to analysis by the BAP method (Kainuma *et al.*, 1981; Matsunaga & Kainuma, 1986), which evaluates the degree of gelatinization of starch by using β-amylase and pullulanase. The index of retrogradation of starch used throughout this paper is the change in degree of gelatinization of starch obtained by the above method.

Statistical analysis

The data set was composed of the values taken for 16 variables: CW, F, RS and CM at small, medium and large compression levels and at rupture for the 84 gel samples examined. The data were subjected to factor analysis (principal factor method) using an NEC personal computer (PC 9801 RX21) and a multivariate analysis program (Microsystems Co. Ltd., Japan) after standardization by Z-conversion. Regression analysis

was carried out on the above data and on the data for the degree of gelatinization using the same program package.

RESULTS AND DISCUSSION

Changes in mechanical properties of starch gels in the course of storage

Changes in mechanical properties of starch gels during storage are illustrated in Fig. 1. The plots are based on means: 95% confidence intervals are not indicated because of the small variations. Changes in compression work required to cause rupture of the gels are shown in Fig. 1(A). The compression work increased with storage period and starch concentration. The degree of change was largest in PO, followed by TA, CO and WH in that order. Change in compression work with storage time of WH gels was slight. The rupture force increased with storage and starch concentration, similar to the case of compression work (Fig. 1(B)). The difference in degree of change among starch species was also similar to the case of compression work. The increase in compression

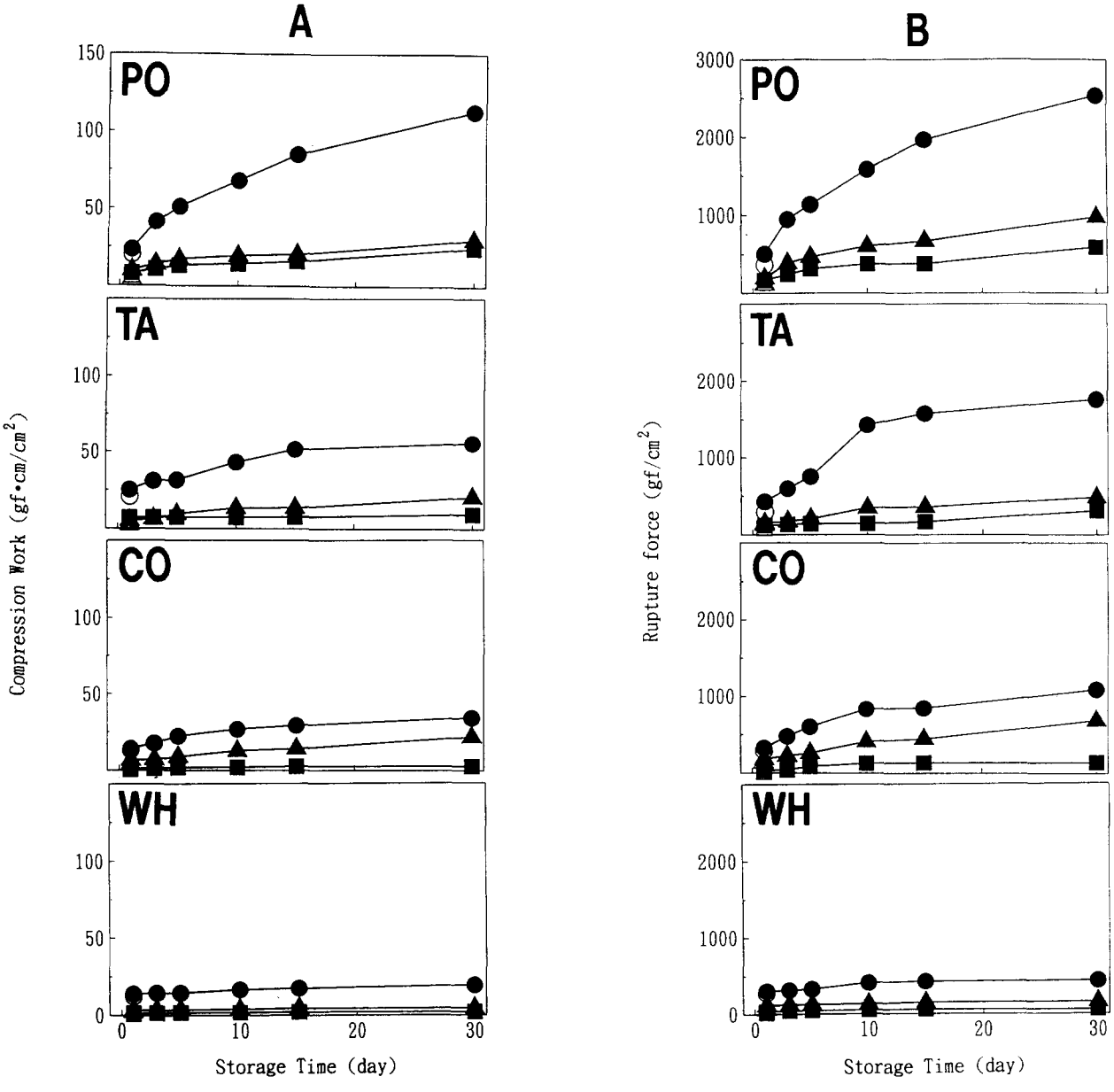

Fig. 1. Changes of mechanical properties of starch gels as a function of storage time. A–D denote the mechanical parameters of compression work (CW), rupture force (F), resiliency (RS) and compressibility (CM), respectively. PO: —■—, 10%; —▲—, 15%; —●—, 19%. TA: —■—, 16%; —▲—, 20%; —●—, 25%. CO: —■—, 7%; —▲—, 10%; —●—, 14%. WH: —■—, 7%; —▲—, 12%; —●—, 17%. □, △, ○: storage at 20°C for 1 day.

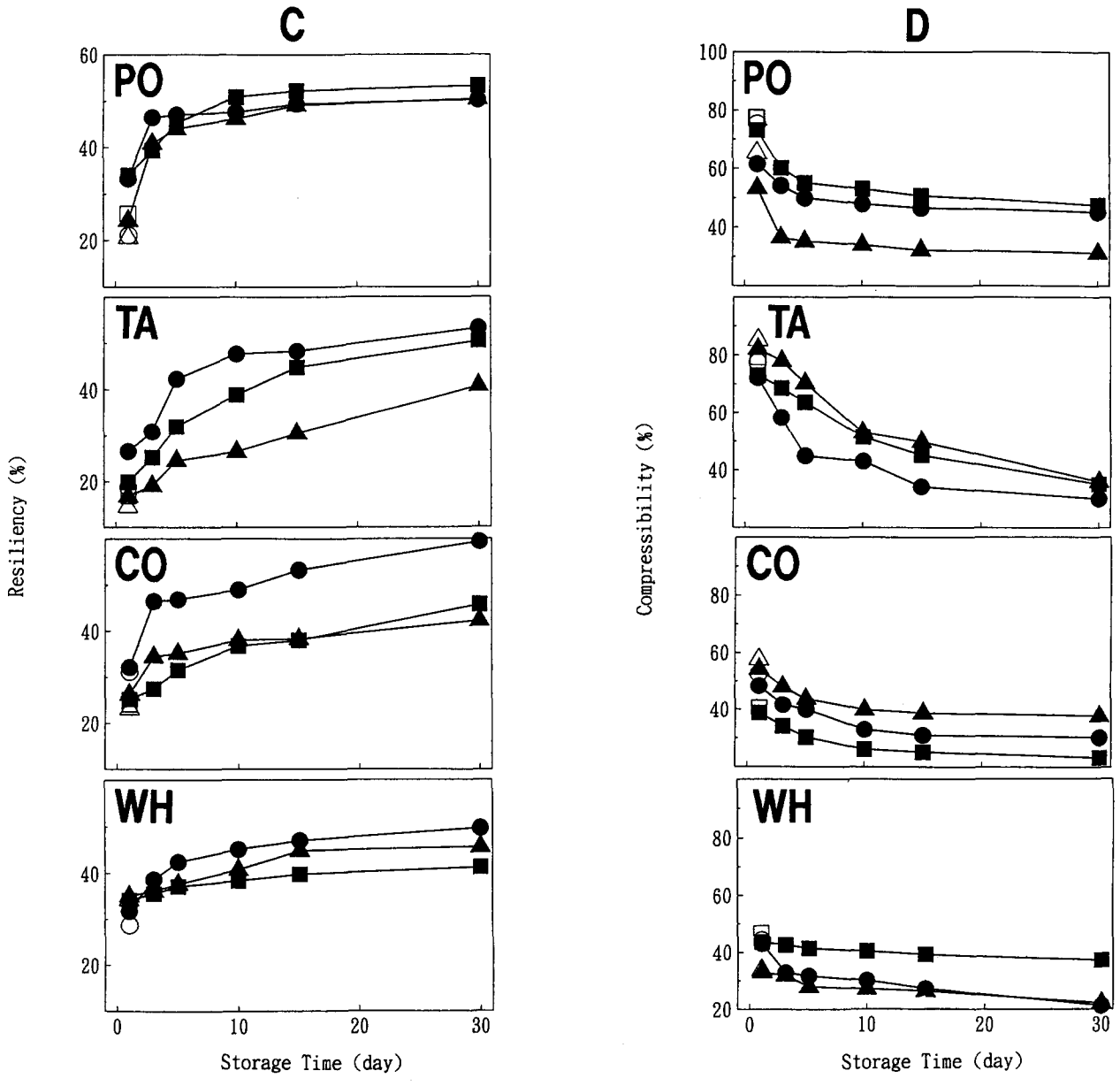

Fig. 1. *Continued.*

work and rupture force with storage period was not proportional linearly to starch concentration, on the whole. Changes in resiliency at rupture of the gels are shown in Fig. 1(C). Gel resiliency increased with storage period: the increase was changeable, depending on the starch species, similar to the cases of compression work and rupture force. Starch concentration diversely affected the increase with storage period. Compressibility decreased with storage period (Fig. 1(D)). The degree of this decrease was changeable among the starch species, similar to the case of compression work, rupture force and resiliency, except that TA exhibited the largest change. The decrease in compressibility and the increase in resiliency with storage time were significant in the first 5 to 10 days of storage; in contrast, compression work and rupture force changed gradually over the periods of storage.

Evaluation of textural characteristics of starch gels

The force–deformation curves of the starch gels examined appeared to fall into nine groups, as shown in Fig. 2. These nine curves are different in rupture force, initial slope of the compression curve, the compressibility and the decompression pattern. Such differences in the force–deformation curves indicate that complete characterization of the properties of gels, 84 gel samples examined, cannot be accomplished successfully by examining data from the rupture test alone, and suggest that mechanical data at different levels of compression

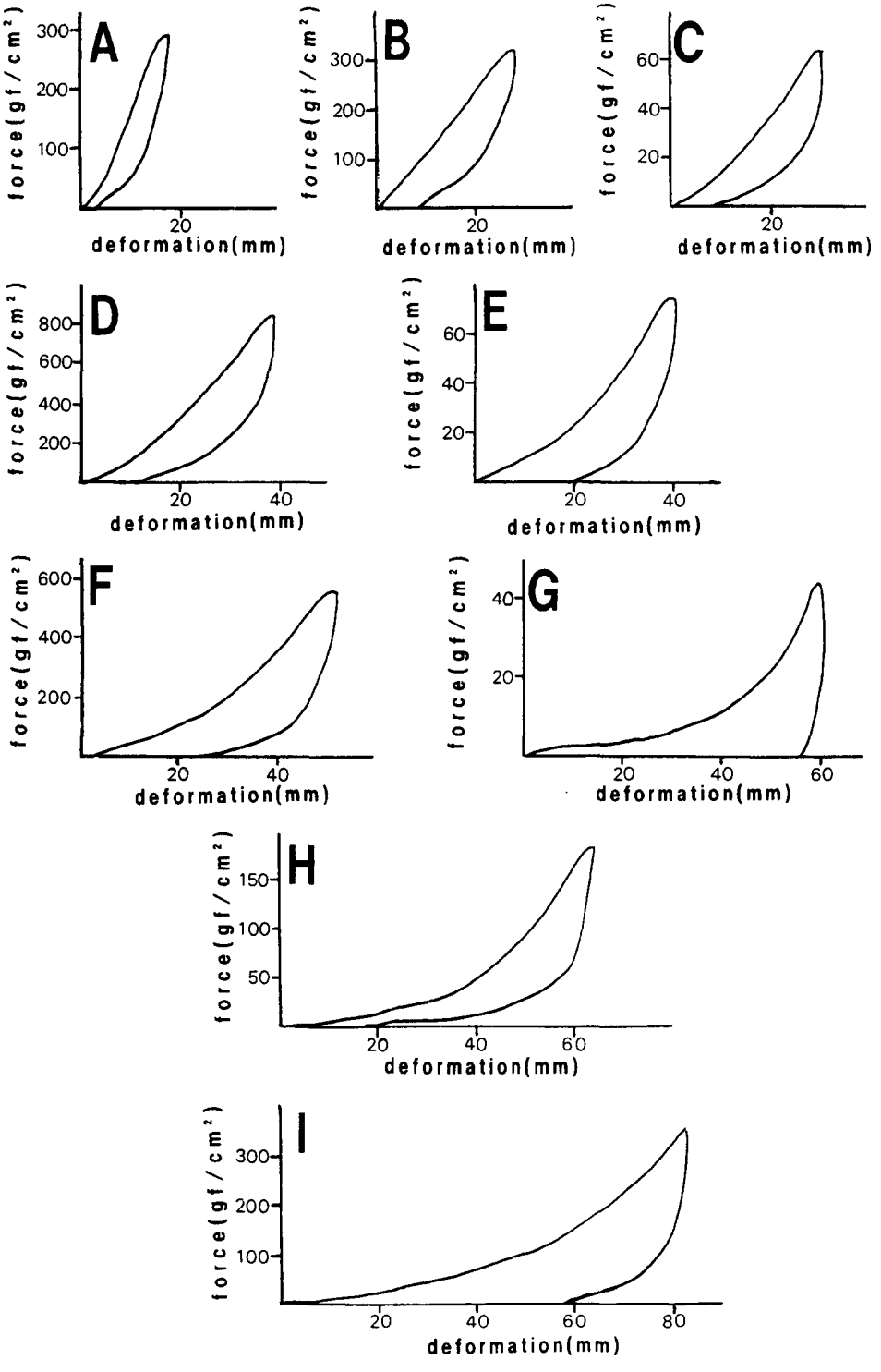

Fig. 2. Force–deformation curves of starch gels from the compression–decompression test at rupture.

up to rupture are necessary. Thus, compression–decompression tests at small, medium and large compression levels were carried out to measure the mechanical parameters of the gels at different levels of compression.

The factor loadings after varimax rotation obtained in the procedure of factor analysis are shown in Table 2. Three factors were retained: the cumulative variance from these factors accounted for 97·0% of the total cumulative variance. The factor loadings represent correlations between the factor and mechanical parameters — the higher the value, the more highly correlated the factor with mechanical properties. Mechanical attributes that load high on factor 1 were CW and F of small compression level to rupture; CM of small compression level to rupture loaded high on factor 2;

Table 2. Factor loadings after varimax rotation[a]

Mechanical properties	Factor loading		
	Factor No. 1	Factor No. 2	Factor No. 3
CW			
small	0·932[b]	0·180	0·223
medium	0·961[b]	0·121	0·181
large	0·963[b]	0·091	0·100
rupture	0·973[b]	−0·056	0·187
RS			
small	0·358	−0·403	0·814[b]
medium	0·367	−0·419	0·819[b]
large	0·298	−0·475	0·808[b]
rupture	0·326	−0·487	0·738[b]
CM			
small	−0·005	0·953[b]	−0·238
medium	−0·021	0·950[b]	−0·278
large	0·030	0·955[b]	−0·281
rupture	0·061	0·935[b]	−0·298
F			
small	0·959[b]	−0·129	0·235
medium	0·959[b]	−0·130	0·232
large	0·958[b]	−0·126	0·221
rupture	0·955[b]	−0·140	0·231

[a]Number of factors at varimax rotation = 3. Factor contributions: No. 1 = 7·798; No. 2 = 4·524; No. 3 = 3·172.
[b]Factor loadings higher than ±0·722.

and RS of small compression level to rupture loaded high on factor 3. As described before, CW, F, RS and CM correspond to toughness, hardness, elasticity and fracturability, respectively. Therefore, it was construed from the results of factor loadings that factor 1 relates to the hardness and toughness of the gels; factor 2, to the fracturability; and factor 3, to the elasticity. The factor scores obtained at the last stage of the factor analysis procedure are shown in Table 3. In order to facilitate the comparison of gel properties among all the samples, the data in Table 3 were plotted with factors 1, 2 and 3 as the *X*-, *Z*- and *Y*-axes. This choice of factors for the axes provides the best visualization.

Figure 3 shows the diagrammatic representation of the gel samples in three dimensions. The lengths of the axes correspond to the values of the factor scores, where the scales were represented only in A (19%), B (25%), C (14%) and D (17%). The full and dotted circles define the locations of samples in positions on the surface and under the surface of the plane of the *X*- and *Y*-axes, respectively. The gel samples were defined by the numbers in the circles, 1–7, each of which defines the storage time of 1–30 days shown in Table 3. The three-dimensional diagram of the factor scores of the PO gels (Fig. 3(A)), showed that the change in elasticity is remarkable at the concentrations of 10% and 15% (decrease on ageing) and the hardness and toughness is significant at 19% (increase on ageing). In TA gels (Fig. 3(B)), the main changes were the decrease in elasticity and increase in fracturability at 16% and 20% and the increases in fracturability, hardness and toughness at 25%, with the lapse of time. In CO gels (Fig. 3(C)), hardness and toughness increased with starch concentration and storage period, while the WH gels showed changes in elasticity (Fig. 3(D)). These results demonstrate that the texture of starch gels changes with ageing and that these changes are affected by species and by the concentration of starch. The three-dimensional representation techniques employed in the present study may provide a method for evaluating the texture of starch gels quantitatively.

Relationship of retrogradation to mechanical properties of starch gels

Figure 4 shows changes of the degree of gelatinization of starch gels with time by means of the BAP method: i.e. retrogradation curves. The starting concentrations of the starch samples correspond to the minimum concentration required to set a self-supporting gel in each starch sample. The changes in the first five days were remarkable on all curves. The rate of retrogradation was changeable with the concentration of starch. The order of decreasing retrogradation rate was 15%, 19% and 10% in PO (Fig. 4(A)), 20%, 16% and 25% in TA (Fig. 4(B)), 10%, 7% and 14% in CO (Fig. 4(C)), and 7%, 17% and 12% in WH (Fig. 4(D)).

Thus, the rate of retrogradation did not vary simply in proportion to the concentration of starch. Especially, in the case of WH, the starch concentration did not affect the rate of retrogradation significantly in the concentration range from 7% to 17%. Sakai *et al.* (1976) investigated the effect of starch concentration on the retrogradation of some starch pastes in the range from 2·5% to 30%. They showed that potato starch exhibited concentration-dependent retrogradation; that is, potato starch paste retrograded at a slower rate below 10% concentration but retrograded at a rapid rate above 20% concentration. The retrogradation of cereal starches were almost independent of concentration from 5% to 30%. These results partly justify the present results showing the dependence of the retrogradation rate on starch concentration.

Whistler (1953) reported that corn starch exhibited the fastest rate of retrogradation followed by wheat, potato and tapioca starches, when each starch paste of 2% concentration was stored at 0–2°C. Maezawa and Okubo (1963) examined the separation of water from the pastes as one of the phenomena of retrogradation and demonstrated that corn starch exhibits the highest rate followed by wheat, tapioca and potato starches, when each starch paste of 6% concentration was stored at 5°C. These orders are not the same as we obtained in the work reported here: the discrepancy may come from

Table 3. Factor scores for starch gels

Starches	Number	Storage (days)	Temperature (°C)	Factor score		
				Factor No. 1	Factor No. 2	Factor No. 3
PO, 10%	1	1	20	−0·354	2·300	−0·160
	2	1	5	−0·546	2·328	1·033
	3	3	5	−0·508	1·363	1·423
	4	5	5	−0·405	1·173	1·633
	5	10	5	−0·411	1·166	2·230
	6	15	5	−0·381	0·912	2·235
	7	30	5	−0·062	0·669	2·442
PO, 15%	1	1	20	−0·529	0·563	−0·556
	2	1	5	−0·466	−0·142	−0·243
	3	3	5	−0·216	−0·516	0·389
	4	5	5	−0·244	−0·406	1·163
	5	10	5	−0·109	−0·462	1·244
	6	15	5	−0·083	−0·430	1·470
	7	30	5	0·590	−0·530	1·453
PO, 19%	1	1	20	0·459	1·450	−0·600
	2	1	5	0·608	1·054	−0·155
	3	3	5	1·176	0·558	0·802
	4	5	5	1·658	0·177	0·508
	5	10	5	2·871	0·063	0·349
	6	15	5	3·658	−0·160	0·113
	7	30	5	4·834	−0·496	−0·538
TA, 16%	1	1	20	−0·458	1·847	−0·600
	2	1	5	−0·470	1·610	−0·475
	3	3	5	−0·520	1·440	−0·179
	4	5	5	−0·600	1·145	0·255
	5	10	5	−0·677	0·545	0·635
	6	15	5	−0·744	0·178	1·114
	7	30	5	−0·678	−0·000	1·794
TA, 20%	1	1	20	0·291	2·454	−2·271
	2	1	5	−0·061	1·974	−2·115
	3	3	5	−0·077	1·820	−1·749
	4	5	5	−0·045	1·046	−1·355
	5	10	5	0·129	0·028	−1·321
	6	15	5	−0·057	0·076	−0·328
	7	30	5	−0·068	−0·411	0·840
TA, 25%	1	1	20	0·233	2·259	−0·460
	2	1	5	0·463	1·986	−0·404
	3	3	5	0·828	−0·069	−1·006
	4	5	5	0·900	−0·267	−0·385
	5	10	5	1·948	−0·590	−0·655
	6	15	5	2·147	−0·804	−0·053
	7	30	5	2·387	−0·973	0·459
CO, 7%	1	1	20	−0·644	−0·787	−0·348
	2	1	5	−0·658	−0·854	−1·270
	3	3	5	−0·710	−0·962	−0·954
	4	5	5	−0·685	−1·080	−0·810
	5	10	5	−0·661	−1·255	−0·705
	6	15	5	−0·663	−1·255	−0·568
	7	30	5	−0·893	−0·972	0·615
CO, 10%	1	1	20	−0·260	0·593	−1·099
	2	1	5	−0·250	0·391	−0·961
	3	3	5	−0·438	0·401	0·193
	4	5	5	−0·598	0·430	1·324
	5	10	5	−0·207	−0·062	0·587
	6	15	5	−0·177	−0·075	0·765
	7	30	5	0·221	−0·378	0·723

Table 3.—*continued*

Starches	Number	Storage (days)	Temperature (°C)	Factor score		
				Factor No. 1	Factor No. 2	Factor No. 3
CO, 14%	1	1	20	−0·028	0·186	−0·705
	2	1	5	0·061	−0·289	−0·911
	3	3	5	−0·011	−0·165	0·674
	4	5	5	0·133	−0·131	1·044
	5	10	5	0·322	−0·494	0·889
	6	15	5	0·534	−0·653	0·878
	7	30	5	0·828	−0·714	1·018
WH, 7%	1	1	20	−0·706	−0·307	−0·869
	2	1	5	−0·709	−0·497	−0·861
	3	3	5	−0·755	−0·501	−0·607
	4	5	5	−0·768	−0·542	−0·498
	5	10	5	−0·792	−0·530	−0·335
	6	15	5	−0·908	−0·380	0·299
	7	30	5	−0·995	−0·326	0·723
WH, 12%	1	1	20	−0·621	−1·021	−0·883
	2	1	5	−0·666	−0·970	−0·598
	3	3	5	−0·679	−0·988	−0·495
	4	5	5	−0·673	−1·213	−0·498
	5	10	5	−0·703	−1·173	−0·247
	6	15	5	−0·747	−1·097	0·165
	7	30	5	−0·788	−1·179	0·393
WH, 17%	1	1	20	−0·054	−0·986	−1·599
	2	1	5	−0·085	−0·958	−1·324
	3	3	5	−0·160	−1·053	−0·869
	4	5	5	−0·192	−1·087	−0·500
	5	10	5	−0·162	−1·015	−0·031
	6	15	5	−0·192	−0·993	0·330
	7	30	5	−0·276	−0·986	0·950

the different starch concentrations used and/or the conditions of gelatinization.

The correlation coefficients between the changes of degree of gelatinization by the BAP method (retrogradation rate) and the changes of each mechanical parameter of the gels are shown in Table 4. The use of all data (84 samples) in regression analysis gave relatively high correlation coefficients for RS. With the use of data for cereal starches of CO and WH (42 samples), no parameter was significant in the correlation. However, with the use of data for root or tuber starches of PO and TA (42 samples), RS and CM were given high correlation coefficients. These results suggest that, in the case of root or tuber starch gels, RS and/or CM may be an index for estimating the progression of retrogradation.

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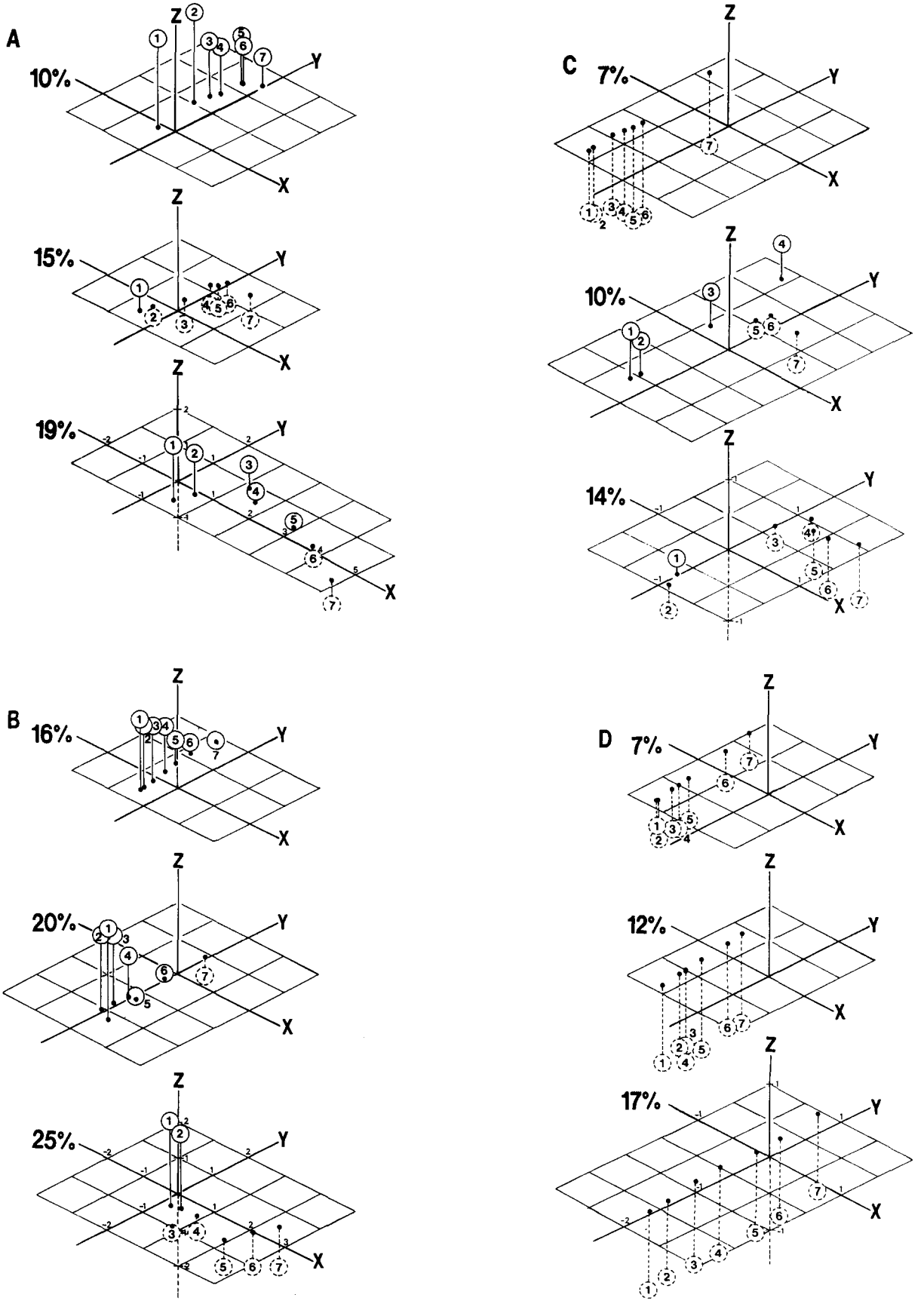

Fig. 3. Three-dimensional representation of gel samples. The coordinate axes of X, Y and Z represent the factors 1, 3 and 2, respectively. A–D denote the gels from potato (PO), tapioca (TA), corn (CO) and wheat (WH), respectively. The numbers of sample are the same as shown in Table 3.

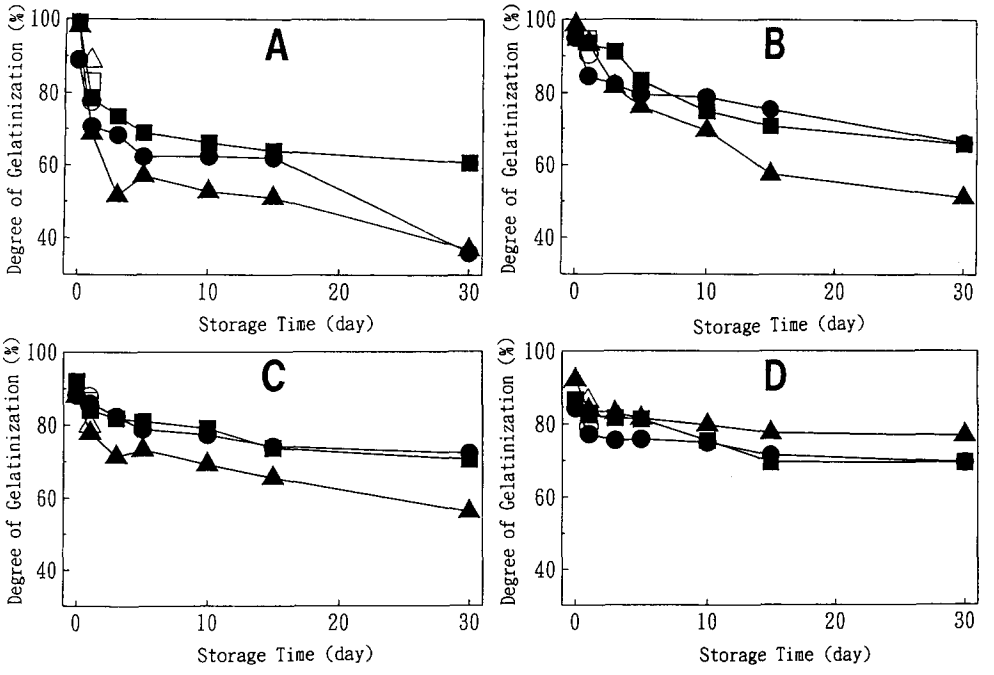

Fig. 4. Changes of the degree of gelatinization of starch gels as a function of storage time. A–D denote the starch species of potato (PO), tapioca (TA), corn (CO) and wheat (WH), respectively. A: —■—, 10%; —▲—, 15%; —●—, 19%. B: —■—, 16%; —▲—, 20%; —●—, 25%. C: —■—, 7%; —▲—, 10%; —●—, 14%. D: —■—, 7%; —▲—, 12%; —●—, 17%. □, △, ○: storage at 20°C for 1 day.

Table 4. Correlation coefficients between changes of the degree of gelatinization and changes of each mechanical parameter

Parameter	Sample	Correlation coefficient		
		PO and TA ($N = 42$)	CO and WH ($N = 42$)	All ($N = 84$)
CW	Small	−0·381	−0·330	−0·438
	Medium	−0·400	−0·350	−0·454
	Large	−0·331	−0·377	−0·403
	Rupture	−0·475	−0·369	−0·508
RS	Small	−0·770	−0·679	−0·744
	Medium	−0·791	−0·655	−0·747
	Large	−0·790	−0·563	−0·713
	Rupture	−0·737	−0·486	−0·632
CM	Small	0·721	0·083	0·403
	Medium	0·752	0·114	0·409
	Large	0·805	0·165	0·415
	Rupture	0·795	0·245	0·392
F	Small	−0·510	−0·404	−0·535
	Medium	−0·509	−0·417	−0·536
	Large	−0·509	−0·450	−0·541
	Rupture	−0·510	−0·421	−0·536

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