

Textural Properties and Structures of Wheat and Maize Starch-Gum Mixed Gels During Storage

Ji-Young Song, Young-Chang Kim¹, and Malshick Shin*

Department of Food and Nutrition and Biofood Research Center, Chonnam National University, Gwangju 500-757, Korea

¹School of Life Sciences and Biotechnology Research Institute, Chungbuk National University, Cheongju, Chungbuk 360-763, Korea

Abstract Effects of commercial and lab-generated gellan gums on the textural properties, structure, and aging of wheat and maize starch gels were investigated using a rapid visco-analyzer (RVA), rheometer, scanning electron microscope (SEM), and X-ray diffractometer. Gellan and guar gums increased the peak and final viscosities, but xanthan gum and gum arabic reduced them. The maize starch had higher breakdown viscosity than the wheat starch, regardless of the type of gum. The hardness of all starch gels increased during storage, but their cohesiveness and springiness decreased. The degree of the gel hardness showed higher in maize starch than in wheat starch and the effect of gum addition had a difference with gum type. The wheat starch-guar and -gellan gum mixed gels showed higher elasticity and cohesiveness after storage. The starch-gellan gum mixed gels had dense and stable network structures, and were well maintained even after 7 days of storage. Most of the gums had anti-aging effect on X-ray diffraction pattern of starch gels.

Keywords: gum, wheat starch, maize starch, gel texture, aging

Introduction

Starch is a widely used additive in various food products, and functions as a stabilizer, thickener, gelling agent, etc (1). Starch is composed of linear and branched polymers called amylose and amylopectin, respectively. The linear amylose leaches out from swollen granules during gelatinization and forms gel with 3-dimensional network structures. The functional properties of gels are not only affected by the starch to water ratio, but also by the temperature, and heating and stirring rates during gel preparation (2). When starch is heated in sufficient water to gelatinize, its crystalline structure is lost and an increase in viscosity is observed. Starch gel texture is affected by amylose content, chain length, the molecular structure of the starch, and additives (3-5).

The blends of native starch and gums have been used in the modern food industry to modify and control the texture, improve moisture retention, and control water mobility, and eating quality of food products (6). Many studies have been carried out to explain the various reactions that occur in starch-gum mixtures and gum dispersions (7-17). Sikora *et al.* (11) reported that gelation of starch in solution of xanthan gum proceeds under water deficiency conditions and consistency of gels non-linearly depended on gel composition. Christianson *et al.* (15) stated that gums, through interactions with amylose, affected the gelatinization and aging of starch. The starch-hydrocolloid mixtures with different types and concentrations exhibited different patterns of swelling, pasting, and gel properties (18,19).

Gums come from a variety of sources (11-14). Guar gum is extracted from *leguminous* shrub and composed of galactomannan with linked β -D-mannopyranose backbone.

Gum arabic is a complex heteropolysaccharide including arabinogalactan family exuded by trees of the genus *Acacia*. Structurally gum arabic is a branched molecules with a backbone formed by β -D-galactopyranosyl unit. Xanthan gum is a complex microbial polysaccharide and consists of D-glucosyl, D-mannosyl, and D-glucuronyl acid residues. Gellan gum has a complex tetrasaccharide repeating sequence of β -D-glucose, β -D-glucuronic acid, β -D-glucose, and α -L-rhamnose and it forms a heat and acid resistant transparent gel.

Research on the rheological and textural properties of the starch-gum mixture pastes and gels, has been mainly focused on the characterization of flow and viscoelasticity by dynamic test (9,10) The stability of gel structure and texture during storage is a very important factor for quality control of starch gel foods. Especially, Korean traditional starch gel foods, which are prepared from 3 kinds of starches from mungbean, cowpea, and acorn show distinct gel structure and unique texture with smoothness, elasticity, and transparency.

In this study, to improve the structure and textural properties of wheat and maize starch gels using low gum concentration (0.1%), lab-generating gellan gum from *Sphingomonas paucimobilis* was compared for its effect on the textural properties and aging of wheat and maize starch-gum mixed gels, and the stabilizing effect in network structure of the selected gum was also observed.

Materials and Methods

Materials Maize starch was obtained from Samyang Genex Corporation (Incheon, Gyeonggi, Korea) and wheat starch was purchased from Sinsong Foods Co. (Nonsan, Chungnam, Korea). The general compositions of the maize and wheat starches, as determined by AACC methods (20), were as follows: 12.0 \pm 0.5 and 11.7 \pm 0.2% moisture, 0.1 \pm 0.0 and 0.2 \pm 0.1% ash, 0.4 \pm 0.0 and 0.3 \pm 0.1% protein,

*Corresponding author: Tel: +82-62-530-1336; Fax: +82-62-530-1339

E-mail: msshin@chonnam.ac.kr

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and 0.2 ± 0.0 and $0.2\pm 0.0\%$ crude lipid content, respectively. The maize and wheat starch amylose contents were determined by the method of Williams *et al.* (21), and to be 28.0 and 20.3%, respectively. The commercial gums, gum arabic (G9752), gum xanthan (G1253), and guar gum (G4129) were purchased from Sigma Chemical Co. (St. Louis, MO, USA). The gellan gum was lab-generated by *S. paucimobilis* ATCC 31461 using the method of Nampoothiri *et al.* (22). The gellan gum contained D-glucose, L-rhamnose, and D-glucuronic acid (2 : 1 : 1) with a molecular weight of 6.8×10^6 Da (18).

Pasting properties by the rapid visco-analyzer The pasting properties of the starches in gum dispersions were characterized using a rapid visco-analyzer (RVA, model 3D; Newport Scientific Pty., Ltd., Narranbeen, Australia) in accordance with the AACC standard method (20). The starch (3 g; 14% moisture basis) was then transferred into the 0.1% gum dispersions (basis on water, 25 g) within the canisters, and stirred manually by rotating the plastic paddle for 15-30 sec to disperse the sample thoroughly. The temperature was maintained at a uniform 50°C for 2 min, and then raised to 95°C during 6 min. The samples were maintained at 95°C for 2 min, cooled to 50°C within 6 min, and then maintained at 50°C for another 2 min. The agitation speed was fixed at 960 rpm for the first 10 sec to ensure the uniformity of the dispersion, and was then decreased to 160 rpm, which was maintained throughout the remainder of the measurements. The initial pasting temperature, peak viscosity (P), trough viscosity (T), final viscosity (F), breakdown viscosity (P-T), and setback viscosity (F-T) were measured.

Preparation and aging of gels The wheat and maize starches (8%, w/v) were suspended in the 0.1% gum dispersions, respectively. Each starch-gum mixture was heated in a boiling water bath for 30 min to make a paste, poured into a cylindrical stainless steel mold (dia. 16×15 mm) on a glass plate, and then covered with another glass plate. After cooling and storing for 1 day at room temperature, the starch gel was taken out of the mold. Several starch gels from the same paste were placed in a polypropylene container that was completely sealed with an automatic top sealing machine (EPA-200BS; Enterline, Gyeonggi, Korea), and were then stored at 4°C for 7 days.

Gel texture The textures of the starch-gum mixed gels were measured for texture profile analysis (TPA) tests using a rheometer (Sun Rheometer Compac-100; Sun Sci. Co., Tokyo, Japan). The gels were compressed 2nd bite test by the rheometer under the following conditions: sample size, dia 16×15 mm; load cell, 2.0 kg; probe diameter, 20 mm; deformation, 50%, and table speed, 60 mm/min. Then, the texture parameters of hardness, adhesiveness, cohesiveness, springiness, brittleness, and gumminess were derived from the instrument software.

Scanning electron microscopy The network structures of the starch-gum mixed gels were observed by scanning electron microscopy (SEM). Small pieces of starch-xanthan and starch-gellan mixed gels (stored for 7 days) were quickly frozen in -70°C liquid nitrogen, dried in a freeze

dryer (Il Shin Lab., Yangju, Korea), and cut into thin slices. The samples were attached to a SEM stub using double-sided cellophane tape. The stub and sample were then coated with gold-palladium and examined and photographed under a scanning electron microscope (JSM-5400; Jeol, Tokyo, Japan) using a 25 kV acceleration voltage and 85 sec phototime at 1,000-fold magnification.

X-ray diffractometry To investigate the recrystallinity of the starch-gum mixed gels during aging, X-ray diffractometry (D/Max 1200; Rigaku Co., Tokyo, Japan) of starch gel powder was accomplished. The 1- and 7-day stored gels (4°C) were dehydrated in 80% ethanol, dried at room temperature, and ground using a homogenizer with passing through a 100 mesh screen. The peak intensity at $2\theta=17^\circ$ in X-ray diffraction of the starch-gum mixed gel powder (<150 μm) was observed. The following conditions were used for analysis: target, Cu-K α ; filter, Ni; voltage, 40 kV; current, 20 mA, and scanning speed, 8°/min.

Statistical analysis The experimental data were analyzed with the Statistical Analysis System software (SAS Institute, Cary, NC, USA). The significance of difference was calculated using Duncan's multiple range tests.

Results and Discussion

Pasting properties by RVA The RVA data for the wheat and maize starches in the 0.1% gum dispersions are shown in Table 1. The changes on the viscosity of starch during gelatinization came from leached soluble carbohydrate and swollen granules (24). Pasting properties of starch were greatly affected by the addition of gums. The rapid increase in the viscosity of starch-gum mixtures was detected as the temperature increased from 50 to 95°C. The increase in viscosity can make the shear forces exerted on the swollen granules in the shear field much larger than those encountered in starch slurry (15).

The initial pasting temperatures of the wheat and maize starch suspensions decreased with the addition of gum (0.1%), and the pasting viscosities varied with the type of gum. Some researchers have reported a slight increase in gelatinization onset temperature when starch is heated within gum dispersions, but others have found that gums had little or no effect on the gelatinization temperature of starches (7,25,26). Lee *et al.* (25) suggested that there is a combination of swollen starch particles and effused amylose within the paste, and gums compete with starch for holding the water particles. They also reported that the structure of the gum significantly affects the association between the gum and starch molecules.

The major functions of food applications are different with the type of gums. Xanthan gum and gum arabic used as viscosity enhancer, stabilizer, and emulsifier, but guar and gellan gums used as stabilizer and texturing and gelling agents, respectively. Therefore, on the pasting viscosity of starch in low gum concentration, guar gum and gellan gum showed higher peak and final viscosities, but gum arabic and xanthan gum exhibited lower peak and setback viscosities than others, regardless of starch type. The trends of these viscosities affected rheological and textural characterization of starch-gum mixtures.

Table 1. RVA data of wheat and maize starches in different gum dispersions (0.1%)

	Pasting temperature (°C)	Viscosity (RVU)				
		Peak (P)	Trough (T)	Final (F)	Breakdown (P-T)	Setback (F-T)
W ¹⁾ -Con ²⁾	90.4	243.0	205.6	288.5	37.4	82.9
W-Ara	89.6	226.9	194.0	272.6	32.9	78.6
W-Xan	83.9	232.3	203.1	262.1	29.2	59.0
W-Gua	84.8	280.5	234.6	309.3	45.9	74.7
W-Gel	90.3	276.4	247.8	360.9	28.6	113.1
M-Con	79.9	252.8	177.7	269.1	75.1	91.4
M-Ara	79.7	234.2	174.2	260.1	60.0	85.9
M-Xan	77.4	236.3	189.1	267.8	47.2	78.7
M-Gua	77.5	278.3	206.3	295.7	72.0	89.3
M-Gel	77.5	265.1	213.5	305.1	51.6	91.6

¹⁾W- and M- mean wheat and maize starches, respectively.

²⁾Con, Ara, Xan, Gua, and Gel mean control (no added gum), gum arabic, xanthan gum, guar gum, and lab-generated gellan gum, respectively.

The peak viscosity of starch-guar gum mixture paste increased interactions in the linear guar gum chain and leached soluble carbohydrate around swollen granules. Chaisawang and Suphantharika (27) reported guar gum was more effective than xanthan gum in terms of increasing the peak viscosity of cationic tapioca starch due to its ability to increase the swelling power. An increment in the final viscosity of starch-gellan gum mixture might be due to high gelling power of gellan gum at low concentration after heating (13) and the aggregation between soluble amylose and gellan gum molecule.

Maize starch (91.4 RVU) exhibited higher setback viscosity than wheat starch (82.9 RVU). The total setback viscosity carries with it the possibility of starch retrogradation, most of the gums lowered setback viscosity. The gellan gum increased the setback viscosity in wheat starch, but other gums did not increase it while showing the same trend as was previously seen with rice starch (18). Setback in wheat flour-hydrocolloid systems was augmented by guar gum but xanthan gum showed the opposite effect (26). In this experiment, the xanthan gum also reduced the setback viscosity. These results meant that xanthan gum inhibited gel formation of starch and lowered retrogradation.

In the starch-gum mixture systems, gums produced a variety of effects on viscosities of starches during starch pasting. Especially the lab-generating gellan gum addition increased peak, trough, final, and setback viscosities, and its increased viscosities helped starch-gum interactions to form the structure of paste and gel during gelatinization and cooling.

Textural properties of starch-gum mixed gels with storage

The textural properties of the starch-gum mixed gels stored for 7 days are shown in Table 2. The wheat starch gel showed less hardness, cohesiveness, and springiness, but more adhesiveness, compared to the maize starch gel. This meant that the wheat starch formed a soft, weak, and less elastic gel, while the maize starch formed a brittle and firm gel. The textural properties of the starch-gum mixed gels differed according to the type of gum added. Significant differences ($p < 0.05$) were exhibited for most textural parameters, except for adhesiveness in wheat

starch (with xanthan and gellan gums) and hardness in wheat starch (with gellan gum). The relative concentration of starch and gum affected the hardness of starch-gum mixed gels, with limiting the movement of water molecules and interacting between the hydroxyl group of gum and starch molecules (28). The degree of polymerization and linearity of dispersed particles, and the interactions between molecules in the gel system have an important role in the textural properties including hardness of gel. Alloncle *et al.* (9) have reported there is a quick gelation period in gum-added gels due to the limited movement of water molecules as the gum interacts quickly with the amylose that leaches out of the gelatinized starch granules. Bhattacharya *et al.* (29) reported that springiness decreased and cohesiveness increased in dough with added gum arabic while no difference in hardness was observed. It was different from the results obtained in this study. When it was thought that both xanthan and guar gums increased solid-like behavior of cationic starch mixed gel, many reasons were considered for determining the texture of starch-gum mixed gels (25). Mandala and Bayas (30) reported that a gum acts like a weak gel because it does not interact with amylose in the continuous starch polymers network, but aggregates after being partially concentrated. Although the positive relationship between the starch paste viscosity and the hardness of gels is not clear, it is suggested that the textures of starch-gum mixed gels are affected by the inherent viscosity of gum and pasting viscosity of starch mixture (17,25).

Maize starch-gum mixed gel was observed distinct change in the textural properties, but wheat starch-gum mixed gel was slightly changed. In the case of the wheat starch gels, the hardness increased after the first day of storage, but showed no difference thereafter. The hardness of the maize starch gels gradually increased from day 1 to day 7 of storage. Unlike the wheat starch gels, the cohesiveness and brittleness values of the maize starch gels were higher in day 1 of storage, and then decreased sharply in the 7-day stored gels, except in gels with added gellan gum. The gel network was unstably formed and transformed during storage, because it was thought that starch granular structure was hard to form double helix junction zone.

Table 2. Textural properties of wheat and maize starch-gum mixed gels stored for 7 days¹⁾

	Storage (day)	Hardness (g/cm ²)	Adhesiveness (g)	Cohesiveness (%)	Springiness (%)
W-Con	1	^B 265.2±18.8 ^{fg}	-14.3±2.1 ^c	^A 58.7±5.4 ^c	^A 91.4±6.6 ^b
	3	^A 299.1±27.7 ^{cf}	-13.5±4.1 ^c	^B 53.3±4.7 ^d	^A 91.7±5.9 ^b
	7	^A 292.6±23.9 ^c	-11.0±4.5 ^{bc}	^C 40.6±5.0 ^b	^B 83.4±6.1 ^a
W-Ara	1	^B 276.1±21.1 ^{def}	^A -16.7±1.9 ^c	^A 62.6±3.8 ^{bc}	^A 94.2±6.4 ^b
	3	^A 285.8±9.4 ^f	^{AB} -12.6±6.0 ^{de}	^B 46.9±10.6 ^d	^B 87.7±6.2 ^b
	7	^A 310.1±20.7 ^c	^B -9.7±5.4 ^{abc}	^B 41.3±6.8 ^b	^B 84.9±5.1 ^a
W-Xan	1	^B 286.1±14.0 ^{cdc}	-15.0±4.5 ^c	^A 67.3±5.0 ^b	^A 95.5±7.0 ^b
	3	^{AB} 305.6±31.3 ^{cf}	-13.2±4.5 ^{de}	^B 48.7±9.4 ^d	^B 87.7±7.3 ^c
	7	^A 307.6±18.6 ^c	-13.1±4.2 ^c	^B 52.3±9.7 ^a	^B 84.9±10.9 ^a
W-Gua	1	^C 272.7±12.0 ^{efg}	^A -15.4±3.9 ^c	^A 66.6±3.4 ^b	94.0±7.0 ^b
	3	^B 322.7±9.7 ^{dc}	^A -12.0±4.0 ^{cdc}	^B 63.7±3.7 ^{bc}	91.7±3.1 ^b
	7	^A 324.6±14.0 ^c	^B -10.5±3.7 ^{bc}	^B 61.5±7.0 ^a	92.2±5.5 ^a
W-Gel	1	300.8±19.3 ^{abc}	-11.7±3.1 ^b	67.6±3.5 ^b	^B 90.2±2.5 ^b
	3	338.0±21.2 ^d	-14.2±3.9 ^c	66.5±3.1 ^b	^A 92.7±4.2 ^b
	7	327.2±75.2 ^c	-11.8±5.2 ^c	63.6±12.5 ^a	^A 93.4±6.7 ^a
M-Con	1	^C 302.2±24.1 ^{abc}	^A -9.1±2.6 ^{ab}	^A 76.4±3.2 ^a	^A 93.9±3.4 ^b
	3	^B 367.2±38.2 ^c	^B -6.6±2.3 ^a	^B 27.1±7.5 ^c	^B 75.1±8.5 ^c
	7	^A 464.9±64.5 ^a	^B -6.3±2.2 ^a	^C 13.2±3.6 ^d	^C 59.0±8.4 ^b
M-Ara	1	^C 95.0±30.0 ^{bcd}	-8.4±2.0 ^a	^A 73.5±6.2 ^a	^A 91.6±3.6 ^b
	3	^B 04.1±35.4 ^a	-8.0±2.7 ^{ab}	^B 55.4±20.3 ^{cd}	^B 76.2±10.2 ^c
	7	^A 477.6±71.9 ^a	-8.0±1.9 ^{ab}	^C 16.2±4.6 ^{cd}	^C 64.2±19.4 ^b
M-Xan	1	^C 319.7±29.0 ^a	^A -11.1±2.1 ^b	^A 73.3±7.9 ^a	^A 94.8±5.7 ^b
	3	^B 370.9±24.5 ^{bc}	^A -9.7±3.3 ^{abcd}	^B 56.5±11.9 ^{cd}	^A 93.1±7.4 ^b
	7	^A 469.8±34.1 ^a	^B -6.9±2.4 ^a	^C 13.7±3.8 ^d	^B 62.1±9.3 ^b
M-Gua	1	^C 254.1±14.1 ^e	^A -10.8±1.5 ^{ab}	^A 76.6±8.0 ^a	^A 102.4±10.9 ^a
	3	^B 334.9±30.9 ^d	^A -8.9±2.2 ^{abc}	^B 48.1±16.8 ^d	^B 85.7±14.7 ^b
	7	^A 389.0±43.1 ^b	^B -6.5±2.7 ^a	^C 22.2±3.8 ^c	^C 68.5±11.3 ^b
M-Gel	1	^C 314.9±28.2 ^{ab}	^B -10.0±1.3 ^{ab}	^A 78.4±4.0 ^a	^A 95.9±4.2 ^b
	3	^B 391.6±12.0 ^{ab}	^B -10.8±2.4 ^{bcde}	^A 78.5±4.2 ^a	^A 100.8±6.7 ^a
	7	^A 430.4±78.3 ^{ab}	^A -7.6±2.0 ^{ab}	^B 52.6±18.6 ^b	^B 82.8±13.0 ^a

¹⁾A,B,C Values with similar letters within same sample are not significantly different as storage times ($p < 0.05$); ^{a,b,c} values with similar letters within same storage time are not significantly different as samples ($p < 0.05$).

Gum arabic itself exhibits relatively low viscosity in water and does not form a gel at typical levels (31) and prevented complete gelatinization of starch (14). Gellan gum addition contributed strong conformation between starch molecules and gellan fiber and improved textural properties during storage. The texture of starch-gellan gum mixed gel exhibited higher cohesiveness, springiness, and brittleness, but also longer storability than other gels.

Kim and Yoo (32) reported that the rate of storage modulus (G') increased due to retrogradation of rice starch in a xanthan gum dispersion. Xanthan gum's ability to increase the rate of gelation appeared to be attributed to the phase separation process, as a result of incompatibility phenomena between the starch component and the xanthan gum. However, we found that gellan and guar gums were better sources for starch-gum mixed gel than xanthan gum and gum arabic.

Gel structure added with gellan and xanthan gums by SEM The starch-guar or starch-gellan gum mixed gel, and starch-xanthan or starch-gum arabic mixed gel showed similar structures. The surface structures of the starch-gum

mixed gels with gellan and xanthan gums observed under SEM are shown in Fig. 1. The network structure of the wheat starch gels was more dense and compact than that of the maize starch gels. The cavity size in the gel networks was enlarged during storage. Additions of xanthan gum and gellan gum to the wheat and maize starch gels changed their network structures. Gum addition helped to maintain the gel matrices in starch-gum mixed gel with homogenous network and smoothness in the structure compared to the control. The structure in starch-gum mixed gels showed network formation with small and defined cavities compared to the control when stored for 1 day, regardless of the type of gum. After 7-day storage, the gellan gum mixed gel kept the same dense structure, but the xanthan gum mixed gel showed a rough structure with enlarged cavity size (Fig. 1. B7, C7). Kim and Yoo (32) reported that the network structure of xanthan gum-added rice starch was more stable than that of the rice starch itself because xanthan gum promoted the association of starch granules due to bridging. Gonera and Cornillon (33) also reported that xanthan gum stabilized the shape of starch particles by adsorbing onto the surface of the particles. The thickening

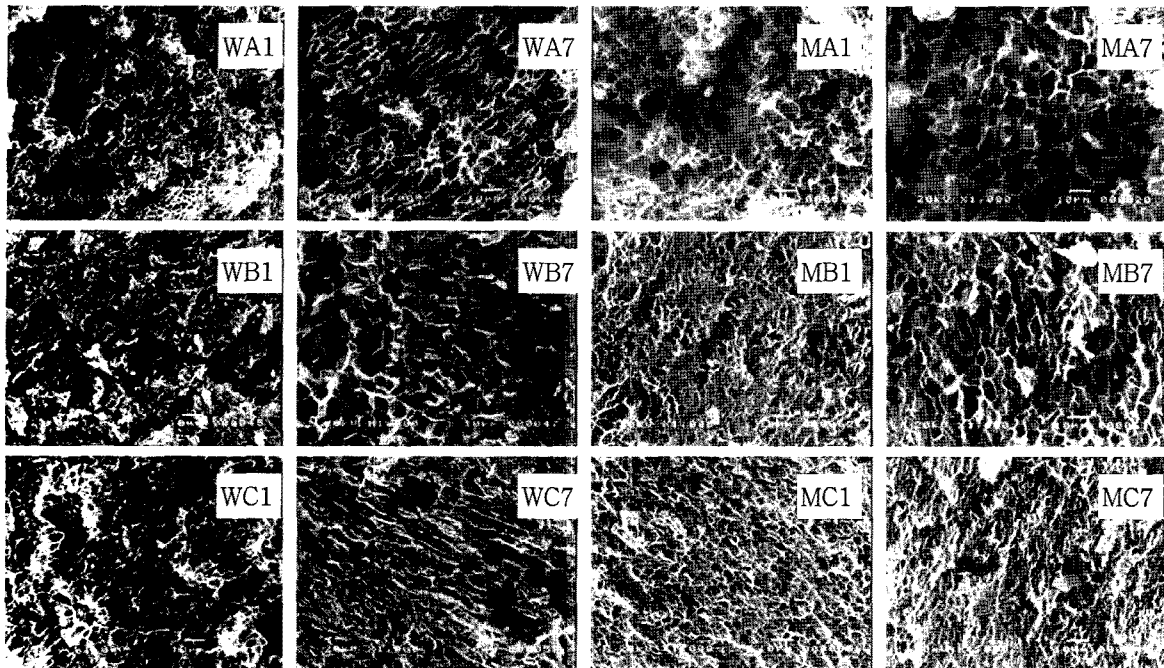


Fig. 1. Scanning electron microphotographs of starch-gum mixed gels stored for 1 and 7 days. Wheat (W) or maize (M) starches and different gums; control (A), xanthan gum (B), and gellan gum (C) were used.

effect of xanthan gum in the starch gel system was not kept stable, but the gelling effect of gellan gum stabilized the gel structure during storage. Gellan gum helped rice starch gel to form the continuous network structure with small cavity and increased its hardness during storage (34). In this study, gellan gum played a role to form stable gel structure in wheat and maize starch gels in accordance with the results of Kwon *et al.* (34). The random coil-helix transition of gellan occurs prior to gelation, and then the aggregation of the helices leads to the formation of junction zones (35). The starch-gellan gum mixed gel might form end-to-end and side-by-side associations with gellan fiber and amylose from granule.

X-ray diffraction X-ray diffraction patterns of starch-gum mixed gels which were changed from amorphous after gelatinization to crystalline during storage are shown in Fig. 2. The native wheat and maize starches as partially crystalline polymers showed A-type pattern, but X-ray patterns were transferred from V-type (shown a peak at $2\theta=20^\circ$) in paste and B-type in gel during aging (36). B-Type crystalline starch showed a distinctive peak at $2\theta=17^\circ$ and the peak intensity became stronger with increasing retrogradation degree. Regardless of starch type, the peak at $2\theta=17^\circ$ was shown in starch-gum mixed gels stored for 7 days, because of recrystallization during storage. The peak at $2\theta=17^\circ$ of maize starch gel was sharper than that of wheat starch gel, but the addition of gums retarded the recrystallinity of both starch gels. Although the X-ray diffractometry is not a sensitive method to determine retrogradation degree of starch, the difference of anti-aging degree was found according to gum type in starch-gum mixed gels. Lee *et al.* (25) observed the aging characteristics of starch gels that resulted from freeze-thaw with DSC, and reported that these gels also had reduced aging with the addition of different gums (guar, xanthan, and alginate).

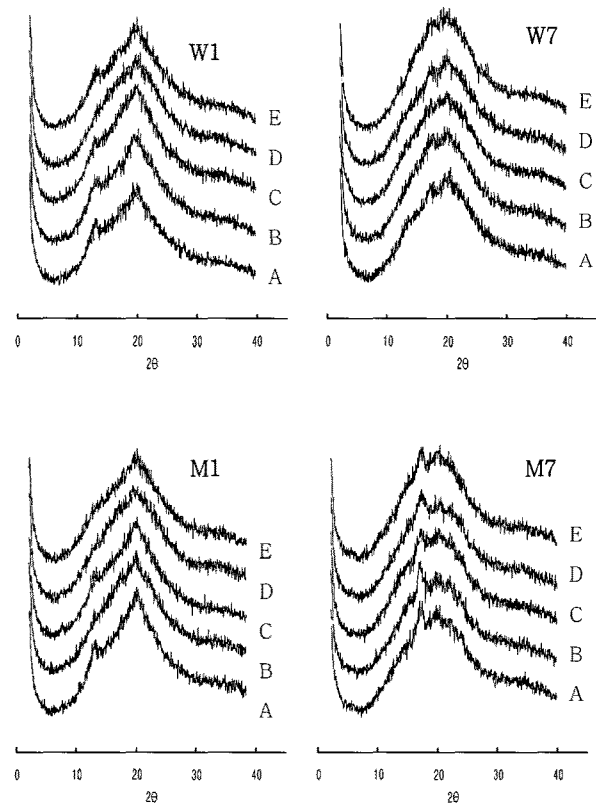


Fig. 2. X-ray diffractograms of starch-gum mixed gels stored for 1 and 7 days. Wheat (W) and maize (M) starches and different gums; control (A), gum arabic (B), xanthan gum (C), guar gum (D), and gellan gum (E) were used.

Funami *et al.* (8) reported that the addition of gum inhibited the short-term retrogradation of starch gel, and rheological changes in the gel were affected by the

molecular weight of the gum, and low weight gums could actually promote long-term retrogradation.

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