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Effect of Acetylated Rice Starch on Rheological Properties of Surimi Sol and Gel

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Abstract The effect of acetylated rice (AR) starch at different concentrations (0, 4, 6, and 8%) on rheological properties of surimi sols and gels was studied. Dynamic frequency sweeps of surimi-AR starch sols at 10°C showed that the magnitudes of storage moduli (G') decreased with an increase in starch concentration while those of tan δ increased, indicating that the effect of AR starch on the viscoelastic properties of surimi sols depended on starch concentration. In general, the G' thermograms of surimi sols showed the similar sol-gel transition pattern and they were also influenced by the addition of AR starch. The presence of AR starch in the surimi gel system reduced the gel strength and expressible moisture content (EMC). Surimi-AR starch gels showed better freeze-thaw stability compared to the control (0% starch concentration). The effect of AR starch on the rheological properties of surimi sols and gels appeared to be related to the swelling ability of starch granules in the presence of limited water available for starch.

Key words: rheology, surimi, acetylated rice starch, thermogram, freeze-thaw stability

Introduction

Surimi is a concentrate of myofibrillar proteins obtained from mechanically deboned fish flesh that has been washed, rinsed, and dewatered in order to remove the sarcoplasmic proteins (1). In the preparation of surimi-based products, various biopolymeric ingredients, such as starches, gums, and non-fish proteins, have been used to improve texture and freeze-thaw stability, as well as to produce finished products economically (2-4). Starch is one of the ingredients that are most widely used in surimi-based products. The addition of starch to surimi is known to modify and control rheological properties in the surimi-starch composite system (5). In general, the rheological properties of surimi sols and gels are influenced by the type and level of starch as well as the dispersion and physical state of starch (6).

Many researchers have studied the rheological properties of surimi sols and gels containing native or modified starches, such as potato (7-9), waxy corn (7, 10), wheat (9, 11), tapioca (12), and rice starches (13). Recently, the dynamic rheological properties of the surimi sols were also studied by many researchers (11-15) because the nondestructive dynamic rheometry can be used to obtain qualitative and quantitative information by dynamic rheological data that relate to molecular changes (16). However, the relationships between acetylated rice (AR) starch and surimi with regarding to rheological properties have not been fully elucidated. In particular, no attempt has been made to study dynamic rheological properties of surimi sol during heating as affected by the addition of AR starch. In general, AR starch has been used to provide freeze-thaw stability in a variety of frozen foods. Therefore, in this study AR starch was selected because it seems to be effective in modifying texture and freeze-thaw stability of surimi.

The objectives of the presented work were to characterize the pattern of the change in dynamic moduli of surimi sols during heating as affected by AR starch with different concentrations using nondestructive dynamic rheometry, and to examine the effect of AR starch concentration on textural properties and freeze-thaw stability of surimi gels.

Materials and Methods

Materials Commercially frozen Alaska pollock (*Theragra chalcogramma*) surimi grade AA was obtained from Alyeska Seafoods Inc. (Seattle, WA, USA). Surimi was cut into approximately 200 or 600 g blocks, vacuum-packed into cryobags, and stored in a freezer (-20°C). Rice starch was obtained from Bangkok Starch Industrial Co., Ltd. (Nakornprathom, Thailand) for preparation of AR starch.

Preparation of acetylated rice starches Acetylated rice (AR) starch was prepared by reacting native rice starch with acetic anhydride according to the procedure of Wurzburg (17) with minor modifications, as described by Shon and Yoo (18). About 500 g of rice starch were dispersed in 750 mL of distilled water and stirred at 30°C to obtain a uniform suspension. The pH of the suspension was adjusted to 8.0 with 4% NaOH. Acetic anhydride (30 g) was added drop-wise to the stirred slurry, while maintaining the pH within the range 7.8-8.2 using 4% NaOH solution during reaction. The reaction was allowed to proceed for 10 min after the completion of acetic anhydride addition. The slurry was then adjusted to pH 5.5 with 15% HCl. After sedimentation, it was washed free of acid, 3 times with distilled water, and then dried in a vacuum drier at 40°C. The dried acetylated starch was ground and then passed through a 100 mesh standard sieve (Chung Gye Inc., Seoul, Korea) with 150 μm openings

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using an analytical sieve shaker (model AS200; Retsch GmbH & Co., Haan, Germany). Percent acetyl content and the degree of substitution (DS) of acetylated rice starch, which were determined according to the method of Smith (19), are 1.74% and 0.068, respectively.

Preparation of surimi sol Frozen surimi (200 g) was partially thawed at 5°C for 3 hr and chopped for 1 min to solubilize the protein with salt (2.0% of surimi weight) in a 1,200 mL mini food chopper (MK-K56; National, Tokyo, Japan) having a 12.0 cm diameter blade, followed by additional chopping for another 1 min with AR starch at different concentrations (0, 4, 6, and 8%). The calculated amount of ice-chilled water was added to adjust final moisture of all batches to 80% in order for the results to reflect the effect of starch added. The final surimi sol was kept below 10°C and was immediately transferred to the rheometer plate for the measurement of dynamic rheological properties.

Preparation of surimi gels Surimi gel was also prepared following the method of Yoo and Lee (5) for the measurements of textural properties. Half-thawed surimi (600 g) was chopped for 2 min with salt (1.5% of surimi weight) in a Hobart silent cutter (model 84145; Hobart Corp., Troy, OH, USA), followed by additional chopping for 8 min with AR starch at different concentrations (0, 4, 6, and 8%). The calculated amount of ice-chilled water was added to adjust final moisture of all batches to 78%. For preparation of heat-induced surimi gels, molded samples were prepared by stuffing the surimi sol into 25 mm Nojax cellulose casings (Viskase Sales Corp., Chicago, IL, USA) and heating at 90°C in a steam cooker (Daishin Stainless Corp., Seoul, Korea) for 20 min. The gel products were cooled in running tap water (13°C) for 20 min and left overnight to equilibrate at 4°C. To determine freeze-thaw stability, samples were subjected to 3 freeze-thaw cycles, each consisting of freezing 5 days at -20°C and thawing 2 days at 4°C.

Dynamic rheological measurements of surimi sol Dynamic rheolgocial measurements of surimi sols (<10°C) were conducted with a TA AR1000 controlled stress rheometer (TA Instruments Inc., New Castle, DE, USA), using a parallel plate system (4 cm diameter) at gap 1,000 μm, as described previously (13). Storage modulus (G') and tan δ (the ratio of G"/G') were measured at 10°C from frequency sweeps over the range of 0.63-62.8 rad/sec at 1% strain. The following temperature sweep from 10 to 95°C was conducted at a heating rate of 1°C/min in order to monitor the change in G' and G" during the heating process at a frequency (ω) of 6.28 rad/sec and 1% strain. The 1% strain was in the linear viscoelastic region. All rheological measurements were conducted in triplicate.

Compression test of surimi gel Compression test was conducted by measuring compressive force and expressible moisture content (EMC) for molded surimi gels with cylindrical shapes of uniform geometry (25 mm diameter × 25 mm height) using an Instron testing machine (model 1011; Instron Corp., Canton, MA, USA). Compressive force was measured as an index of the cohesiveness of the gels at 50 mm/min of cross-head speed and 90% deformation with failure. The first peak was used as the compressive force. The amount of moisture expressed upon compression was calculated in terms of % EMC on a sample moisture content basis (20).

Microscopic examination of ice crystal formation As other means of evaluating the freeze-thaw stability of the gel matrix, ice crystal formation in gels during frozen storage was examined using a light microscope (21). Specimens for microscopic examination were prepared from cooked gel and were stained following the procedure described by Lee (22). The surimi gels were frozen in liquid nitrogen. Sections (20 μm) were cut using a Cryostat (CM 1510; Leica Microsystems GmbH, Wetzlar, Germany). The specimens containing AR starch were stained with a toluidine blue-iodine mixture. On micrography, the voids left as a result of ice crystal formation were observed.

Statistical analysis All results are expressed as mean ± standard deviation. Analysis variance (ANOVA) was performed using the Statistical Analysis System software (version 9.1). Differences in means were determined using Duncan's multiple-range test.

Results and Discussion

Dynamic rheological properties of surimi sol at 10 °C Figure 1 shows changes in storage modulus (G') and tan δ as function of frequency (ω) for surimi-AR starch sols at 10°C. The magnitudes of G' decreased with an increase in starch concentration while those of tan δ increased, indicating that the effect of AR starch on the viscoelastic properties of surimi sols depended on starch concentration. The tan δ values of all surimi-AR starch sol samples, which were in the range of 0.13-0.43 over wide range of frequency, also were higher than the control (0% starch concentration). This means that loss modulus (G") increases much more than G' after adding AR starch to surimi sol. From these observations, it was found that the surimi-AR starch sols displayed weak gel-like behavior, showing a higher elastic character with tan δ values much smaller than one. This tendency is similar to those found in surimi sols mixed with rice starch (13) and sugars (16). Such increase of viscous properties (G") in dependence on starch concentration in the surimi sol state can be explained by a result of interfered cohesion in the surimi sol matrix and also the dilution effect of the starch which is weaker than myofibrillar protein, as described by Yoo and Lee (5).

Storage moduli (G') thermogram of surimi sol The characteristic G' thermograms of surimi-AR starch sols with different starch concentrations are presented in Fig. 2. In the present study only G' changes of surimi-AR starch sols during heating are shown because G' (elastic property), in general, exhibits higher values with a more distinct transition peak than G" (viscous property), as noted by Jung and Yoo (13) and Yoo and Lee (23). Table 1 also shows magnitudes of G' observed during heating: G' at 10°C (G'_{10}), G' at 95°C (G'_{95}), and maximum value of G'

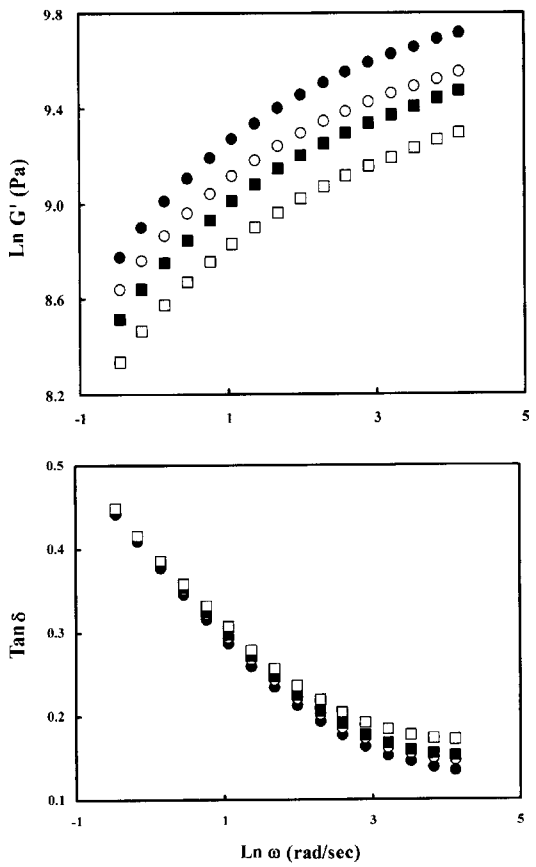

Fig. 1. Plot of ln G' and tan δ vs. ln ω for surimi-AR starch sols as a function of starch concentration at 10°C. (●) 0%, (○) 4%, (■) 6%, (□) 8%.

(G'_{max}). In general, G' values of surimi sols decreased with an increase in starch concentration. The decrease in G' by the addition of AR starch was more pronounced at G'_{10} and G'_{max}, showing the significant differences between G' values of samples. The transition peak temperatures were also found at around 37°C, showing that there was not much difference between the transition peak temperatures of samples. However, the extent of reduction in the height of the transition peak decreased with an increase in starch concentration, indicating that the heights of transition peaks were a function of surimi concentration. The reduction of transition peak by the addition of AR starch may be explained by interfered protein aggregation (20).

The continuous increase in G' values was found in the

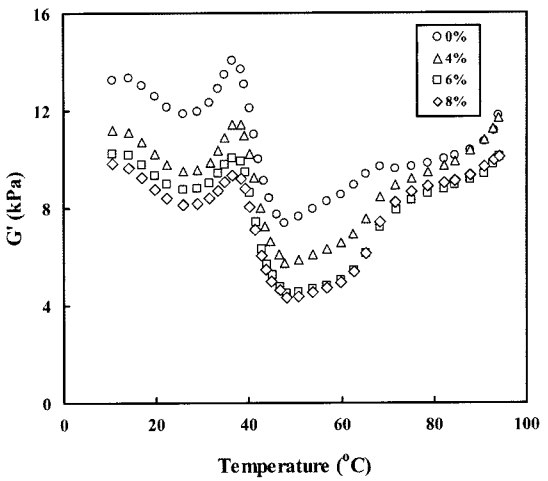

Fig. 2. Changes in G' during heating from 10 to 95°C at 1°C/min for surimi-AR starch sols as a function of starch concentration.

temperature range from 50 to 95°C, showing thermally-induced gel network formation (Fig. 2). The G' values of surimi-rice starch sol samples between 50 and 70°C were much lower than that of the control (0% starch). Such reduction of G' of surimi-rice starch sols can be due to an increased concentration of AR starch which is much weaker than myofibrillar protein, as described previously. When in the surimi-starch composite system the starch granules cannot absorb enough water to produce reinforcement in the gel matrix, they inactively filled into the network and cannot give pressure to the matrix, resulting in a weak gel, as noted by Park (4). He also explained that although the starch granules expand in the surimi-starch composite system, they cannot expand as large as in the starch-water system because the fish protein limits the availability of water. The decrease in G' values of surimi-AR starch sols can be related to the gelatinizing properties of AR starch because acetylation increases the swelling ability of starch granules (7). Therefore, if there is not enough water available for AR starch gelatinization, it could probably weaken the reinforcing effect of the starch granules on the network. In addition, it has been known that starch increases surimi gel strength more effectively at low concentrations (0-3%) than at high concentration (6-9%). In the temperature range of 50-65°C, G' values were maintained nearly constant, indicating that the formation of protein network in the surimi-AR starch composite

Table 1. Values of G' (Pa) at 10 (G'_{10}) and 95°C (G'_{95}), maximum values of G' (G'_{max}), and corresponding temperature for surimi-AR starch sols with different starch concentrations

AR starch concentration (%)	G'_{10} (kPa)	G'_{95} (kPa)	G'_{max} (kPa)	Temperature (°C)
0	12.9±0.56[a1)]	11.2±0.95[a]	13.7±0.70[a]	36.9
4	11.1±0.08[b]	11.7±0.04[a]	11.5±0.10[b]	37.1
6	10.3±0.06[b]	9.0±0.50[b]	10.1±0.02[c]	37.2
8	9.2±0.63[c]	9.1±0.37[b]	8.9±0.09[d]	37.2

[1)]Mean values in the same column with different letters are significantly different ($p<0.05$).

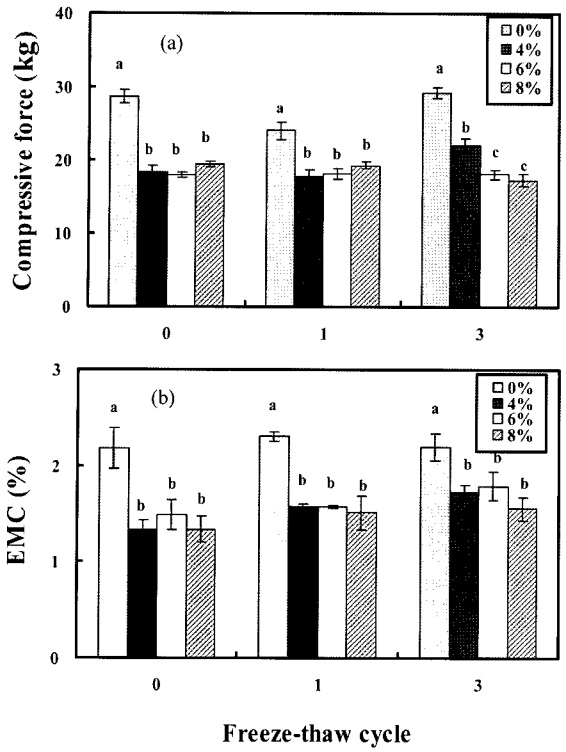

Fig. 3. Changes in (a) compressive force and (b) expressible moisture content (EMC) of surimi-AR starch gels during freeze-thaw. [a-c]Mean values with the different letters within the same treatment are significantly different ($p<0.05$).

system led to constant elastic properties for the surimi sol. Such constant G' values can be due to unswollen (inactive filler) starch granules in protein gel network in the temperature range of 50-65°C (4, 7). However, it was found that there was no particular trend for the G' values (G'_{95}) at 95°C with completion of a network formation. From these observations, it was found that the pattern of thermally induced G' changes at transition was, in general, influenced by the addition of AR starch and depended on the concentration of starch.

Compression test and freeze-thaw stability of surimi gel Figure 3 shows that the compressive force and expressible moisture content (EMC) of surimi-AR starch gels during freeze-thaw. Surimi-AR starch gels with different starch concentrations (4, 6, and 8%) showed lower compressive force values than that of control (0% starch), as reported earlier for surimi gels mixed with modified starches under similar conditions (7, 9). They also had higher water binding ability compared to the control as shown by less EMC but there were no significant differences between EMC of surimi-AR starch gel samples. There were no differences between compressive force values of surimi-AR starch gels, except for 4% starch after 1 freeze-thaw cycle, during freeze-thaw. The compressive force values at 6 and 8% AR starch concentrations also were lower than that at 4%, indicating that the freeze-thaw stability can be decreased at higher AR starch concentrations. Such lower compressive force values can be attributed to unswollen starch granules due

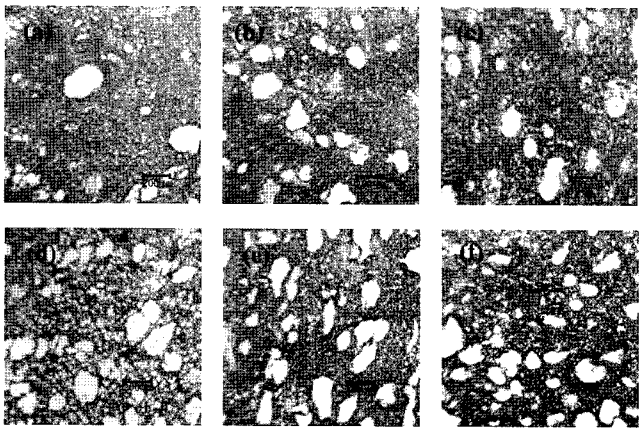

Fig. 4. Photomicrographs of gel matrix after 1 and 3 freeze-thaw (F-T) cycles in the surimi-AR starch gel system (bar= 200 μm). (a) AR starch 4%-1 F-T cycle, (b) AR starch 6%-1 F-T cycle, (c) AR starch 8%-1 F-T cycle, (d) AR starch 4%-3 F-T cycles, (e) AR starch 6%-3 F-T cycles, (f) AR starch 8%-3 F-T cycles.

to limited water available for starch, as discussed previously. Generally, it has been known that acetylated starch is used for longer shelf-life of frozen products, although it does not control the severe expressible moisture (dripping) problem effectively (4). As expected, the EMC of surimi-AR starch gels increased slightly with an increase in freeze-thaw cycle, indicating the surimi-AR starch gels becoming less cohesive with increased freeze-thaw cycle. Such increased EMC after freeze-thaw cycle can be attributed to a reduction in water holding due to contraction of the gel matrix following ice crystal formation. It can be also explained by the surimi gel network with large and numerous ice crystal voids after 3 freeze-thaw cycles compared to 1 freeze-thaw cycle, as shown in Fig. 4. From these observations, it was found that AR starch appears to have better freeze-thaw stability as evidenced by less EMC and less textural changes during freeze-thaw.

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