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Effect of Native and Acetylated Sweet Potato Starch on Rheological Properties of Composite Surimi Sol

– Research Note –

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Abstract

The effects of native sweet potato starch (NSPS) and sweet potato starch modified by acetylation (MSPS) on dynamic rheological properties of surimi sols were investigated by small-deformation oscillatory measurements. Dynamic frequency sweeps of surimi sols at 10°C showed that the addition of NSPS and MSPS resulted in a reduction of storage modulus (G') and loss modulus (G"). The tan δ values (ratio of G"/ G') of all samples were in the range of 0.15～0.54 over a wide range of frequency, indicating that all surimi sols are more elastic than viscous. The characteristic G' thermograms of surimi sols during heating from 10 to 90°C were influenced by the addition of starch. The tan δ values of all samples were maintained nearly constant above 45°C, showing that the G' is proportional to the G" irrespective of starch effects.

Key words: surimi, sweet potato starch, acetylation, rheology, dynamic modulus

INTRODUCTION

Surimi is a concentrate of myofibrillar proteins obtained from mechanically separated fish flesh that has been washed and mixed with cryoprotectants to extend the shelf life during frozen storage. In the preparation of surimi-based products, the addition of native or modified starches to surimi have been used to modify texture and improve freeze-thaw stability, as well as to produce finished products economically (1-3). These products are composite foods in which particulate ingredients, such as starches, gums, and non-fish protein, are incorporated into the continuous phase (protein matrix) (4). Starch, which contributes greatly to the rheological properties of many food products, is an important ingredient that is most widely used to maintain gel strength with a reduced amount of surimi and to improve storage stability in refrigerated or frozen surimi-based products (3). It has also been known that the gelatinization of starch within the surimi gel is strongly influenced by heating, starch swelling behavior, and the type of starch.

There are a number of reports concerning the rheological properties of surimi sols and gels containing native or modified starches (5-11). However, no attempt has yet been made to study rheological properties of surimi sols as affected by the addition of native sweet potato starch (NSPS) and sweet potato starch modified by acetylation (MSPS). In general, it has been known that acetylation is one of the common methods of starch modification and provides stability to retrogradation and freeze-thaw. In this study, both NSPS and MSPS were mixed with surimi to compare dynamic rheological differences between surimi-NSPS and surimi-MSPS composites during heating. The objective of the present study was to examine the addition effect of native and modified sweet potato starches on the rheological properties of surimi sols. In particular, the effect of starches on the thermal gelation characteristics of surimi sols was also investigated by measuring dynamic moduli during heating.

MATERIALS AND METHODS

Materials

Commercially frozen Alaska Pollock (*Theragra chalcogramma*) surimi grade FA was obtained from Alyeska Seafoods Inc. (Seattle, USA). Surimi was cut into approximately 200 or 600 g blocks, vacuum-packed into cryobags, and stored in a freezer (-25°C). Sweet potato starch used in this study was purchased from Keumdeung Agriculture and Fishery Co. (Jeju, Korea). Its proximate composition, as determined according to AOAC methods (12), was: 16.18% moisture, 0.26% protein, 0.49% fat, 0.18% ash and 82.89% carbohydrate (by difference).

Preparation of modifed sweet potato starch

Sweet potato starch modified by acetylation (MSPS) was prepared by reacting native sweet potato starch (NSPS) with acetic anhydride according to the procedure

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of Wurzburg (13) with minor modifications. About 500 g of NSPS was dispersed in 750 mL of distilled water and stirred for 1 hr at 25°C to obtain a uniform suspension. The pH of the suspension was adjusted to 8.2 with 3% NaOH. Acetic anhydride (28.5 g) was added drop-wise to the stirred slurry, while maintaining the pH within the range of 8.1 ~ 8.3 using 3% NaOH solution during reaction. The reaction was allowed to proceed for 20 min after the completion of acetic anhydride addition. The slurry was then adjusted to pH 5.0 with 15% HCl. After sedimentation, it was washed free of acid, three 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 using an analytical sieve shaker (Model AS200, Retsch GmbH & Co., Haan, Germany). Percent acetyl content and the degree of substitution (DS) of MSPS, which were determined according to the method of Smith (14), are 2.36% and 0.091, respectively. The MSPS had moisture, protein, fat, ash, and carbohydrate contents of 12.72%, 0.13%, 0.27%, 0.25%, and 86.63%, respectively.

Preparation of surimi-starch sol

Surimi sol was prepared following the method of Lim et al. (15). Frozen surimi (200 g) was partially thawed at 5°C for 3 hr until it reached -2°C, and then chopped for 1 min to solubilize the protein with salt (2.0% of surimi weight) in a 1200 mL mini food chopper (MK-K56, National, Japan) having a 12.0 cm diameter blade, followed by additional chopping for another 1 min with or without starch (0 and 5% of surimi weight). 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 added starch. The final surimi sol was kept below 10°C and was immediately transferred to the rheometer plate for the measurement of dynamic rheological properties.

Measurement of dynamic rheological parameters

A controlled stress rheometer (AR1000, TA Instruments Inc., New Castle, DE, USA) with a measuring system having a plate-plate geometry (4 cm dia.) at a gap of 1000 μm was used for small-deformation oscillatory measurements. Each surimi sol (<10°C) was transferred to the rheometer plate at 10°C, and the excess material was wiped off with a spatula. The exposed sample edge was covered with a thin layer of light paraffin oil to prevent evaporation during measurements. Storage modulus (G') and loss modulus (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 90°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.

Statistical analysis

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

RESULTS AND DISCUSSION

Dynamic viscoelastic properties of surimi sol

Table 1 shows G', G", and tan δ (ratio of G"/G') at 6.28 rad/sec of all surimi sols at 10°C. Dynamic moduli (G' and G") of surimi-starch (NSPS and MSPS) sols were lower than those of the control (0% starch). Such decrease of dynamic moduli in the surimi-starch sols can be explained by a reduction of surimi protein content by the addition of starch. Yoo and Lee (3) also found that in the surimi-starch composite systems a decrease in dynamic moduli could generally be regarded as a result of the dilution effect of the starch which is weaker than surimi protein. In particular, dynamic moduli of surimi-MSPS were lower than those of surimi-NSPS. This may be due to the weakened surimi sol structure caused by greater water uptake in MSPS compared to NSPS. Such higher water uptake can be attributed to the reduction of interactions between starch chains due to the increase in hydrophilicity of MSPS occurred by the introduction of acetyl groups (16).

The tan δ values of all samples were in the range of 0.15 ~ 0.54 over a wide range of frequency, and there was not much difference of tan δ values (0.27 ~ 0.28) at 6.28 rad/sec between all samples (Table 1). In general, a tan δ<1 indicates predominantly elastic behavior while a tan δ>1 indicates predominantly viscous behavior. This indicates that all surimi sol samples are more elastic

Table 1. Storage modulus (G'), loss modulus (G"), and tan δ at 6.28 rad/sec of all surimi sol samples

Sample	G' (kPa)	G" (kPa)	tan (δ)
Control	13.3 ± 0.57$^{a1)}$	3.60 ± 0.17^{a}	0.27 ± 0.00^{b}
NSPS	11.6 ± 0.11^{b}	3.24 ± 0.05^{b}	0.28 ± 0.00^{a}
MSPS	10.8 ± 0.17^{b}	2.99 ± 0.06^{b}	0.28 ± 0.00^{a}

NSPS, native sweet potato starch; MSPS, sweet potato starch modified by acetylation.

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

than viscous, in good agreement with the results found in other surimi sol composites (8,11). From these observations, it was found that the surimi sol composites displayed weak gel-like behavior, showing a higher elastic character with tan δ values much smaller than one. Similar results were also found in other studies of surimi sol composites (10,11,15).

Thermal gelation of surimi-starch sol

Changes in the storage modulus (G') induced by changes in temperature were compared for the surimi sol samples heated from 10 to 90°C. Thermal gelation curves of surimi sols are presented in Fig. 1. In the present study only G' changes of surimi sols during heating are shown because G' (elastic property) is more responsive to dynamic rheological changes than G" (viscous property), as reported by Jung and Yoo (10) who examined the thermal gelation of surimi-rice starch sols during heating. Table 2 also shows magnitudes of G' observed during heating: G' at 10°C (G'_{10}), G' at 90°C (G'_{90}), and maximum value of G' (G'_{max}). The decrease of G' in the presence of starch was more pronounced at G'_{10} and G'_{max}, showing the significance of differences between G' values for the control and surimi-starch samples. There was also little difference in sol-gel transition patterns between surimi-NSPS and surimi-MSPS. All samples have almost the same transition peak temperature (36.4~36.6°C).

A continuous increase in G' values was found in the temperature range from 53 to 90°C, showing thermally-induced gel network formation (Fig. 1). The G' values of surimi-starch sol samples between 45 and 70°C were much lower than that of the control (0% starch). This tendency is similar to the results of the earlier work by Jung et al. (11). Such reduction of G' of surimi-rice starch sols can be due to the addition of starch which is much weaker than surimi protein, as discussed previously. When in the surimi-starch composite system the starch granules cannot absorb enough water to produce reinforcement in the gel matrix, they inactively fill into the network and cannot give pressure to the matrix, resulting in a weak gel (2). The starch granules cannot expand as large as in the starch-water system due to the competition for water between starch and fish protein. In the temperature range of 66~90°C for the control and 78~90°C for the surimi-MSPS, G' values were maintained nearly constant, indicating that the formation of the protein network led to constant elastic properties for the surimi sol. Such constant G' values of the control and surimi-MSPS can be attributed to the completion of a gel network formation in the lower temperature range in comparison to the surimi-NSPS which shows a continuous increase in G' even at 90°C. Such lower

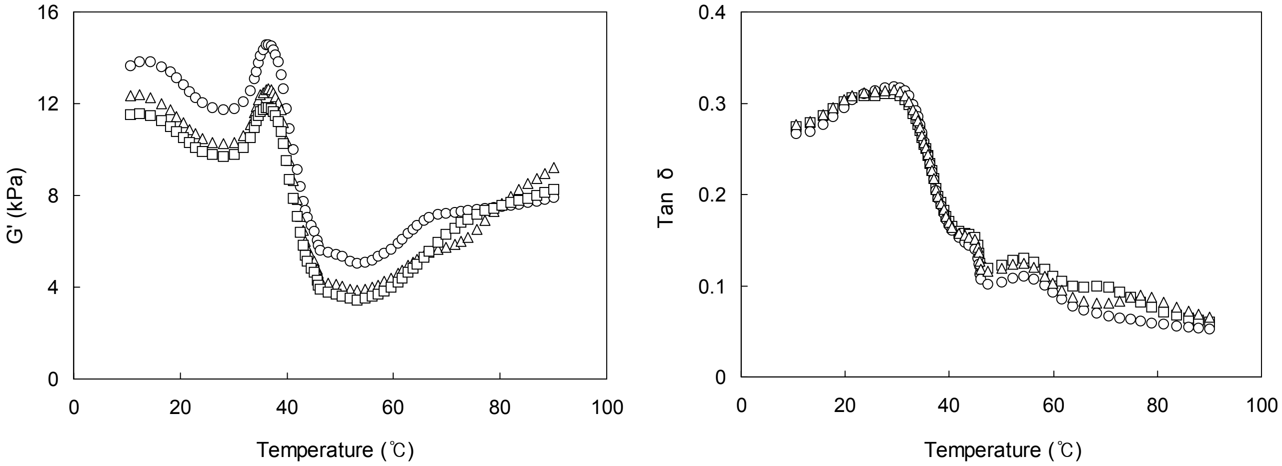

Fig. 1. Changes in G' and tan δ during heating from 10 to 90°C at 1°C/min for surimi sols: (○) control, (Δ) NSPS, (□) MSPS.

Table 2. Values of G' (Pa) at 10 (G'_{10}) and 90°C (G'_{90}), maximum values of G' (G'_{max}), and corresponding temperature for surimi sol samples

Sample	G'_{10} (kPa)	G'_{90} (kPa)	G'_{max} (kPa)	Temperature (°C)
Control	$13.7\pm0.10^{a1)}$	8.27 ± 0.32^{b}	14.7 ± 0.13^{a}	36.4 ± 0.23^{a}
NSPS	12.3 ± 0.08^{b}	9.15 ± 0.10^{a}	12.7 ± 0.06^{b}	36.6 ± 0.00^{a}
MSPS	11.4 ± 0.18^{c}	7.98 ± 0.39^{b}	11.7 ± 0.14^{c}	36.2 ± 0.00^{a}

NSPS, native sweet potato starch; MSPS, sweet potato starch modified by acetylation.
1)Mean values in the same column with different letters are significantly different ($p<0.05$).

G'_{90} values of surimi-MSPS, when compared to surimi-NSPS, can also be related to the gelatinizing properties of MSPS because the acetylation increases the swelling ability of starch granules, as noted by Shon and Yoo (16). Therefore, if there is not enough water available for the gelatinization of MSPS, it could probably weaken the reinforcing effect of the starch granules on the network. The composite reinforcing effect of starch could not be achieved if the protein matrix was filled with native starch with higher concentration (>4%) and modified starch with hydrophilic substituents (4). From these observations, we surmise that the pattern of thermally induced G' changes at transition was responsible for the addition of starch and the state of starch.

Changes in tan δ values with temperature were also compared for all samples heated from 10 to 90°C, as shown in Fig. 1. The transition from sol to gel seemed to take place at around 45°C, showing that tan δ values above 45°C were maintained nearly constant and were much lower than those below 45°C. This means that the surimi sol samples were no longer in a sol state above 45°C due to the formation of their protein network structure. There were also no noticeable changes in tan δ values above 45°C among samples, indicating that all samples above 45°C show similar elastic properties without regard to the state of starch. Kong et al. (8) also explained that once the protein network structure was formed, the G' was assumed to be proportional to the G" irrespective of starch effects. Starch granules in surimi protein are gelatinized with the transfer of water from the protein to the starch granules. From these observations, the effect of sweet potato starches (NSPS and MSPS) on the dynamic rheological properties of surimi sols appeared to be related to the swelling ability of starch granules in the presence of limited water available for starch.

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