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Effect of Sugars on Thermal Gelation of Surimi Sols

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Abstract Surimi samples were prepared with the addition of three different sugars (sucrose, glucose, and fructose) at 8% and the thermal gelation of surimi sols was investigated by small-deformation oscillatory measurements of storage (G') and loss (G") moduli. The magnitudes of G' at 10°C were much greater than G" over the entire range of frequency (ω), with little dependence on ω. In general, G' values of surimi sol containing sucrose during heating (from 10 to 95°C) was pronounced than those of glucose and fructose, showing the following order: sucrose>glucose>fructose. The transition peaks of surimi sols containing sugars were in the temperature range of 34.8 -37.4°C.

Keywords: surimi, rheology, sugar, thermal gelation, storage modulus

Introduction

Surimi is concentrated myofibrillar proteins obtained from mechanically deboned fish flesh that has been washed, rinsed, and dewatered in order to remove the sarcoplasmic proteins (1). Generally, the extended frozen storage of surimi is made possible by the addition of sugars and sugar alcohols, alone or mixed at 8% w/w to dewatered fish meat, as the cryoprotectants. The main concern in the manufacture of surimi-based products is the retention of myofibrillar functional properties with respect to gel-forming ability (2, 3). Sugars have been known to play an important role in the gel stability of proteins and polysaccharides. Recently, many researchers have studied the effect of sugars on gelation properties of biopolymer dispersions, such as proteins (4-7) and polysaccharides (8-12), during heating or cooling by small-deformation oscillatory measurements.

Thermal scanning rheometry provides a useful tool to monitor the structure formation during gelation of food proteins. Changes in the gelation, which is influenced by protein sources, protein concentration, temperature, pH, and interactions with other food components (e.g., polysaccharides and sugars), can be examined by rheological measurements (13). Thermal gelation of surimi protein has been investigated by examining changes in rigidity with a thermal scanning rigidity monitor (TSRM) by an Instron testing machine (14, 15) and also in the viscosity by a rotational viscometry (Yoo and Lee, 1994). However, TSRM does not give pure shear conditions due to the bottom effect (16) and the rotational viscometry also does not allow continuous measurement of the viscosity without breaking structural elements formed in the surimi sample on heating. Recently, the rheological viscoelastic properties of the surimi sol were studied using small-deformation oscillatory measurements because the nondestructive (small-strain) dynamic rheometry can be used to obtain qualitative and quantitative information by dynamic moduli that relate to molecular changes. Especially, dynamic rheological monitoring during heating has the potential to be an extremely valuable and widely used instrumental method for helping to understand the chemistry of food protein gelation (16). However, only a few studies have been reported on thermal gelation of surimi sol using the dynamic rheological measurement (17-20). They found that the gelation of surimi sol depended on the type of starch (17), the type of additive (18, 19), and pH (20). However, no attempt has been made to study the thermal gelation characteristics of surimi sol as affected by sugars. The changes in dynamic moduli during heating may provide valuable information on the effect of sugars on the sol-gel transition pattern of the surimi protein because gelation is a dynamic process.

The objective of this study was to examine the effect of sugars (sucrose, glucose, and fructose) on the thermal gelation characteristics of surimi sol as a function of the type of sugar by measuring dynamic moduli during heating.

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Materials and Methods

Preparation of experimental surimi A washed minced meat was prepared from fresh Alaska pollock (Theragra chalcograma) fillets (less than 2 days old) which were purchased from a local fish wholesale market (Noryangin Fisheries Ltd., Seoul, Korea). The surimi processing was conducted based on the method described by Lee (1) with slight modifications to adapt to the pilot plant available. The fillets were minced using a chopper (Model 4812, Hobart Manufacturing Co., Ohio, USA) having 4 mm diameter perforations. The minced meat was washed twice in wash tanks with chilled water (10°C) for 10 min each cycle using a meat/water ratio of 1:4 (w/v). After each wash, the slurry was strained through a metal screen covered by cheesecloth for 10 min, and dewatered using a hydraulic press. To this washed minced meat, 8% commercial sugars, sucrose (Yakuri Chemicals Co., Kyoto, Japan), glucose (Shinyo Pure Chemicals Co., Osaka, Japan), and fructose (Yakuri Chemicals Co., Kyoto, Japan), were added on a meat weight basis. Each mixture

was chopped for 2 min using a silent cutter (Model 84145, Hobart Manufacturing Co., Ohio, USA). The prepared surimi was vacuum-packed into cryobags (600g) and stored at -20°C.

Preparation of surimi sol Surimi sol was prepared following the method of Yoo and Lee (21). Half-thawed surimi (200 g) at -2°C was chopped for 2.5 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. The calculated amount of ice-chilled water was added to adjust the final moisture of all batches to 80% in order for the results to reflect the effect of sugars. The final surimi sol was kept below 10°C and was immediately transferred to the rheometer plate for the measurement of dynamic rheological properties.

Dynamic rheological measurements Dynamic rheological measurements were conducted with a TA AR1000 controlled stress rheometer (TA Instruments Inc., New Castle, DE), using a parallel plate system (4 cm dia.) at a gap of 500 μm. 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 (G'), loss (G"), and complex (η*) moduli were measured at 10°C from frequency sweeps over the range of 0.63 - 63 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 1 Hz and 1% strain. The 1% strain was in the linear viscoelastic region. All rheological measurements were conducted in duplicate.

Results and Discussion

Dynamic shear properties Figure 1 shows changes in G', G", and η* as function of ω for a representative surimi sol sample at 10°C. G' and G" increased with increase in ω, while η* decreased steeply. G' was much higher than G" at all values of ω, with a slight dependency of ω. As shown in Fig. 2, the surimi sols with addition of different sugars (sucrose, glucose, and fructose) displayed weak, gel-like behavior, showing a higher elastic character with G' > G". This tendency is similar to that found in gelatin (15), corn starch (19), pectin (22), and oxidized starch mixed with sugars (23). Such weak gel-like behavior of surimi sols can be explained by the preferential exclusion of sugars from the protein surface due to the effects of sugars in increasing the surface tension of water (24-26). Back *et al.* (27) and Dierckx and Huyghebaert (6) also observed that hydrophobic interactions between pairs of hydrophobic groups are stronger in sucrose solution than in pure water. Therefore, it may be concluded that sugars, which increase the surface tension of water, may act to stabilize proteins by favoring solute exclusion from the protein surface and by enhancing the strength of intramolecular hydrophobic interactions, as indicated by MacDonald and Lanier (28). In particular, G' and G" values were more pronounced with sucrose in comparison to glucose and fructose, indicating that sucrose has the greatest stabilizing effect on the protein. In the order of increasing G' and G" values of surimi sols containing different sugars, sugars were ranked as: sucrose > glucose > fructose, although there was little difference between glucose and fructose.

Effect of sugars on dynamic moduli during heating In order to examine the effect of the various types of sugars on dynamic viscoelasticity thermograms, the pattern of changes in G' and G" as a function of temperature were monitored (Fig. 3). There was a little decrease in dynamic moduli up to around 25°C, followed by a rapid increase, reaching a transition peak at around 35°C. The transition patterns in respect to G' and G" were similar to the results of the earlier work by Yoo and Lee (21). Such abrupt increase in G' and G" may be associated with a setting phenomenon due to the entanglement of partially unfolded actomyosin molecules, as explained by Montejano *et al.*

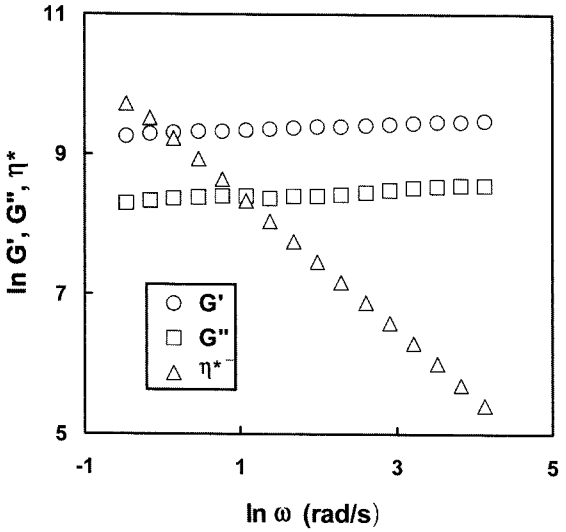

Fig. 1. Plot of ln ω vs. ln G' (○), ln G" (□), and ln η* (△) for a surimi sol sample containing sucrose at 10°C.

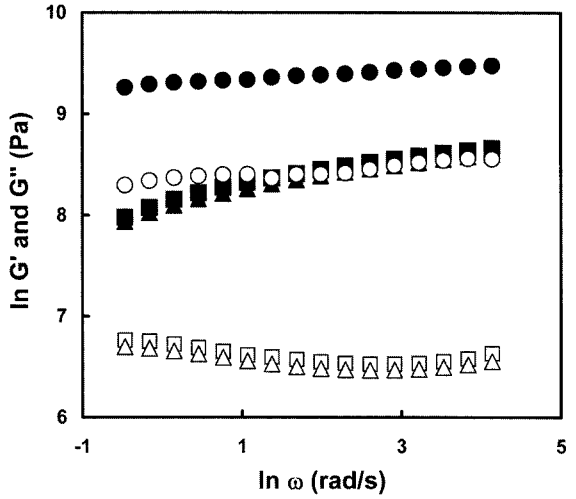

Fig. 2. Ln (G', G") vs. ln ω for surimi sols as a function of sugar type at 10°C: (●, ○) sucrose, (■, □) glucose, and (▲, △) fructose. Closed symbol: G', open symbol: G".

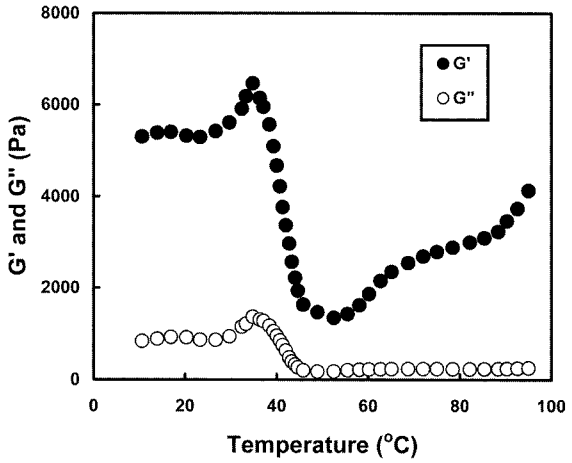

Fig. 3. Changes in G' (●) and G" (○) during heating from 10 to 95°C at 1°C /min for a surimi sol sample containing sucrose.

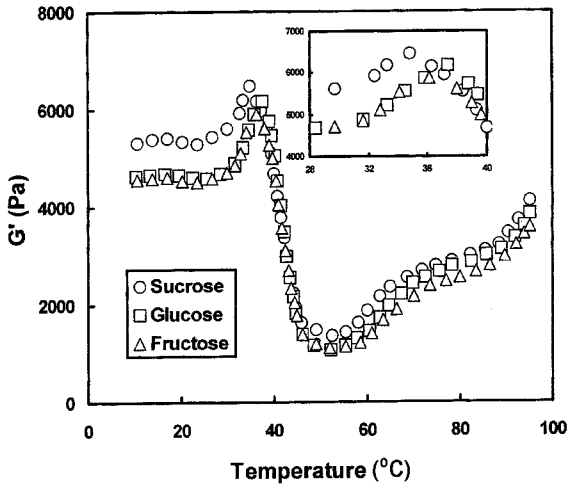

Fig. 4. Changes in G' during heating from 10 to 95°C at 1°C/ min for surimi sol samples as a function of sugar type.

(29). Immediately after the transition peak, there was a rapid decrease in the dynamic moduli up to 50°C. Such decrease in dynamic moduli can be attributed to sol-gel transformation where the dynamic moduli dropped before they rose as the protein sol started to aggregate into a network formation with water release due to thermal syneresis (21). The G' values above 50°C increased with increase in temperature, while G" did not. The increase in G' values above 50°C appeared to be due to the transition from a loose network to a compact network formation in which the surimi sol was no longer in a sol state, as indicated by Yoo and Lee (21). As shown in Fig. 3, G' also showed higher values with a more distinct transition peak than G", suggesting that G' is more responsive to rheological changes during heating (21) and G" is of less importance than G' due to its low value with respect to G' (30). Based on these observations, in this study it was decided to measure only G' in order to investigate the effect of the various types of sugars on dynamic rheological properties on surimi sol during heating.

The characteristic G' thermograms of the surimi sols containing different types of sugars are presented in Fig. 4. The magnitudes of G' observed during heating, G' at 10°C (G'_{10}), G' at 95°C (G'_{95}), and maximum value of G' (G'_{max}) are also shown in Table 1. In general, G' values of surimi sol containing sucrose were higher than those of glucose and fructose in which there was little difference, showing the following order: sucrose > glucose > fructose. The transition peaks also occurred between 34.8 and 36.1°C. The observed results followed similar trends to those found in rotational viscometric (21), thermal scanning rigidity monitor (29, 31), and dynamic viscoelastic measurements (21, 31). As shown in Table 1, the transition peak temperatures of surimi sol decreased in the following order: sucrose > fructose > glucose, indicating that surimi sol containing sucrose has the greatest ability to stabilize the surimi protein due to the enhanced hydration of protein and the increased protein network formation (Hamann, 1992; Yoo and Lee, 1994). From these results, in general, it was found that the dynamic moduli of surimi sols during heating were influenced by the type of sugar.

Table 1. Values of G' (Pa) at 10 (G'_{10}) and 95°C (G'_{95}), maximum value of G' (G'_{max}) and corresponding temperature

Sugar	G'_{10}	G'_{95}	G'_{max}	Temperature (°C)
Sucrose	5305	4133	6466	34.8
Glucose	4639	3850	6168	37.4
Fructose	4565	3600	5880	36.1

Gekko and Koga (32) examined the mechanism of stabilization of collagen structure by different sugars and found that protein stabilization by sugars could be attributed to the enhanced hydration of the protein. They also found that the ability of sugars to stabilize protein was related with the mean number of equatorial hydroxyl (e-OH) groups of sugars. Uedaira *et al.* (33) also reported that sugar molecules having a large number of e-OH groups have stronger stabilizing effects on the structure of water surrounding the sugar molecule. The average number of e-OH groups is smallest in ribose (2.1), and increases in the order fructose (3.0), mannose (3.3), xylose (3.5), glucose (4.6), sucrose (6.3), and maltose (7.2) (34). On the basis of dynamic rheological properties in surimi sols containing different sugars (Table 1 and Fig. 4), the overall G' values during heating increased with the increase of the average number of e-OH groups in the following order: sucrose > glucose > fructose. This result indicates that the stabilizing ability of surimi protein structure can be related to the number of e-OH in sugars. This tendency is in good agreements with results found in collagen-sugar (32), gelatin-sugar (5, 35) and rice starch-sugar (36) mixtures in terms of their stabilizing effects. Therefore, in our study the observed effect of sugars on the thermal gelation of surimi sol during heating can be explained by the number of equatorial -OH groups of sugars.

Conclusions

The dynamic rheological data of G' and G" as a function of ω for surimi sols containing different sugars at 10°C showed that the surimi sol samples displayed weak, gel-like behavior with G' much greater than G" at all values of

ω applied. In particular, G' and G" values of surimi sol containing sucrose were more pronounced than those of glucose and fructose. G' for surimi sol samples in the heating process (from 10 to 95°C) increased in the following order: sucrose > glucose > fructose, indicating that sucrose had the greatest stabilizing effect on the enhanced hydration of surimi protein. The mean number of equatorial hydroxyl (e-OH) groups of sugar molecule was found to play an important role in the stabilization of surimi protein structure. G' values of surimi sols containing different sugars were of the same order of magnitude as the mean number of e-OH groups of the sugars.

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