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Thermal Gelation Characteristics of Composite Surimi Sol

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Surimi sols were prepared with addition of ingredients (egg albumin, starch, carrageenan and oil) at varying levels and monitored for changes in the apparent viscosity during heating by rotational cylindrical viscometry. The sol–gel transitions occurred at 40 °C for egg white- and starch-incorporated surimi sols, 38 °C for carrageenan and 46 °C for oil. Except for carrageenan, the addition of ingredients reduced the viscosity which varied with the type and level of ingredient. Egg albumin-incorporated surimi sol followed most closely the pattern of viscosity changes in the control surimi sol while starch did least. Rotational viscometry with a cylindrical spindle appeared to be simple and yet sensitive in continuous monitoring of viscosity changes in the composite surimi sols during heating.

Introduction

Relationships of composite characteristics to rheological properties of surimi sol and gel were studied by Lee and Kim (1). In this study, the composite characteristics were varied by dispersing varying amounts of ingredients in a surimi sol, as well as by altering the physical state of the dispersed phase through heating. Evaluation of the rheological properties of surimi sol is useful not only in predicting textural properties of gel, but also in characterizing the flow behavior and extrudability of sol during the fabrication process. Yoo and Lee (2) evaluated the rheological properties of surimi sol and its relationship to the textural properties of heat-induced gel with respect to the effect of ingredients in the composite system. The viscosity of surimi sol by rotational cylindrical viscometry correlated well (r = 0.87) with the textural properties (compressive and shear force) of heat-induced surimi gel. Changes in rheological properties of proteins and starches during thermal transition have been studied by several researchers (3–9). Thermal transitions of various protein sols were investigated by examining changes in the rigidity with a thermal scanning rigidity monitor (TSRM) (3–8), while changes in the viscosity of starches during heating were monitored using a Brookfield rotational viscometer (9). However, no comprehensive study has been reported on the thermally induced rheological changes in the composite surimi sol system except the study of Burgarella *et al.* (5) who examined changes in the rigidity of protein-incorporated surimi during thermally induced sol–gel transformation using a TSRM device. The TSRM dynamic test is useful for continuous monitoring of rheological changes which result from the protein sol–gel transformation during heating. However, the TSRM does not give pure shear conditions due to the bottom effect generated by the movement of the blade pushing the sample (5,10). Recently, the sol–gel transition pattern of the surimi protein was studied using the rheometric viscoelastic measurement (11). However, no rotational cylindrical viscometry has been used under defined shearing conditions to monitor the continuous changes in viscosity of the surimi sol during heating, with respect to the effect of various ingredients in the composite system.

The objectives of the study were to characterize the changes in the viscosity of the composite surimi sol during heating using rotational cylindrical viscometry and to determine how composite characteristics influence the pattern of the viscosity change.

Materials and Methods

Egg albumin in a spray-dried form (Monark Egg Products, Kansas City, MO), starch (a mixture of 40% Melojel and 60% Fregex, National Starch, Bridgewater, NJ), Mazola corn oil (Best Foods, Englewood Cliffs, NJ), and carrageenan-ME621 (FMC, Philadelphia, PA) were used as representative ingredients in the surimi composite. Melojel is composed of unmodified 25% amylose and 75% amylopectin corn starch, while Fregex is hydroxypropylated, modified 18–28% amylose and 72–82% amylopectin tapioca starch. The level of each ingredient was selected on the basis of the commercial usage. Surimi prepared from Alaska pollock (*Theragar chalcogramma*) was supplied by Icicle Seafood (Seattle, WA). All percent values are given by weight.

Sample preparation

Half-thawed surimi (−2 °C, 200 g) was chopped for 1.5 min to solubilize the protein with salt (1.5% of surimi weight) in a 1700 mL food processor (Big Oskar, Sunbeam Appliance

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Co.) having a 14.6 cm diameter blade, followed by additional chopping for another 1.5 min with ingredients at different levels. The calculated amount of ice-chilled water was added to adjust the final moisture level of all formulae to 780 g/kg in order for the results to reflect the effect of ingredients. The final surimi sol was kept below 8 °C. The viscosity measurements of surimi sol were evaluated within 5 min after chopping.

To evaluate the thermal behavior of ingredients themselves, 100 g/L egg albumin, 100 g/L starch and 40 g/L carrageenan slurries were prepared by dispersing their powders in deionized water at room temperature.

Thermorheological measurements

Changes in the viscosity of the sols during heating were monitored continuously using a Brookfield digital viscometer (Model HBTD, Brookfield Engineering Lab, Stoughton, MA) with a water-jacketed small holder (diameter 1.9 cm; length 6.2 cm). Heating of the sols was done at a rate of 2.2 °C/min by running heated water through the water jacket of the sample holder. The water was heated using a Brookfield constant temperature-controlled water bath (Model EX-100). Surimi sol was loaded into a sample holder with a small spatula and vacuumed at 4 mmHg using a vacuum packer (Model GK 120, Smith Equipment Co., Clifton, NJ) to remove air bubbles. A thermocouple was placed in the center of the sample to monitor the temperature increase during heating. A rotational cylindrical spindle having 3.2 mm diameter and 30 mm depth was used at a shear rate of 0.83 s^{-1} (5 rpm) which brought about a small shear deformation in the sols. For the viscosity measurement, apparent viscosity (η) was measured using the following equations:

$$\tau = (F \cdot \%M)/(r\,A),\ \dot{\gamma} = (2\pi r \cdot \text{rps})/\delta, \text{ and } \eta = \tau/\dot{\gamma} \quad \text{Eqn [1]}$$

where τ = shear stress (Pa); $\dot{\gamma}$ = shear rate (s^{-1}); F = full torque capacity (5.7×10^{-2} N·m); M = torque reading; r = radius of spindle; A = surface area in which a spindle contacted sample; rps = revolution per second; δ = gap where shear motion was involved (specified at 1 mm).

To evaluate viscosity development during heating, the viscosity changes in the control surimi sol were monitored at three different heating rates, 0.5 °C/min, 1.1 °C/min and 2.2 °C/min. These heating rates were adjusted by regulating the water bath temperature using a variable autotransformer (type 3PN0101, Staco Energy Products Co., Dayton, OH).

In the dynamic rheological measurements during heating, magnitudes of storage modulus (G') and loss modulus (G'') were measured on a rheometer (Carri-Med CSL 100, TA Instruments, New Castle, DE) using a cone and plate (2°, 4 cm diameter) at 6.3 rad/s and 1% strain. A temperature sweep was performed from 10 °C to 85 °C at a rate of 2.2 °C/min. The Carri-med software (version 4.3) was used on an IBM PS/2 30 to calculate G' and G''.

Results and Discussion

Effect of heating rates on viscosity changes during heating

The thermograms showing viscosity changes in surimi sols as a function of temperature at three different heating rates are shown in **Fig. 1**. The pattern of viscosity changes is found to be similar to that of shear modulus measured by TSRM (3). The transition peaks all occurred at 40 °C regardless of heating rates, while the times to reach the peak were 18, 36 and 80 min for 2.2 °C/min, 1.1 °C/min and 0.5 °C/min, respectively. This suggests that the occurrence of transition is both temperature- and time-dependent. The overall viscosity decreased with an increase in heating rate throughout the temperatures tested, reflecting the adequate residence time is required for viscosity development which is both temperature- and time-dependent. The lag phase at the heating rate of 2.2 °C/min was extended longest from 10 to 35 °C before the viscosity reached its peak. A sharper transition peak was observed at a high heating rate (2.2 °C/min). This is believed to be a result of a strong temperature dependency of transition in a short residence time. In our preliminary study, it was noticed that the viscosity of surimi sol dropped at around 70 °C when the water released from the sol due to thermal syneresis. This occurred during sol–gel transformation. Based on the above results, it was decided to measure viscosity changes in the composite surimi sol at a heating rate of 2.2 °C/min from 8 °C (starting sol temperature) to about 70 °C.

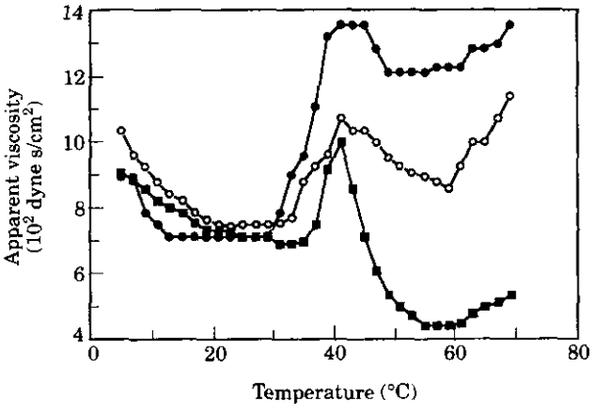

Fig. 1 Changes in apparent viscosity of surimi sol at three heating rates. (●) 0.5 °C/min; (○) 1.1 °C/min; (■) 2.2 °C/min

Dynamic viscoelasticity thermograms

Hamann (11) found that the patterns of dynamic viscoelasticity (G' and G'') thermograms generated by a Bohlin rheometer were similar to those of the TSRM shear modulus and energy loss thermograms, respectively (3). In the present study, it was decided to compare the viscosity thermograms with the dynamic viscoelasticity (G' and G'') thermograms for a given surimi sol. **Figure 2** shows the sol–gel transition patterns in respect to G' and G'' which are similar to the results of the earlier work by Hamann (11). Transition peaks occurred at around 35 °C, where G' showed a more distinct transition than G'', suggesting that G' is more responsive to rheological changes during heating. Although there was a similarity in the pattern of thermorheograms between dynamic viscoelasticity measurement (G') and rotational viscometric/TSRM measurements, it was not as close as what was observed between rotational viscometric and TSRM measurements. This must be a result of the difference in the operating principles of dynamic viscoelas-

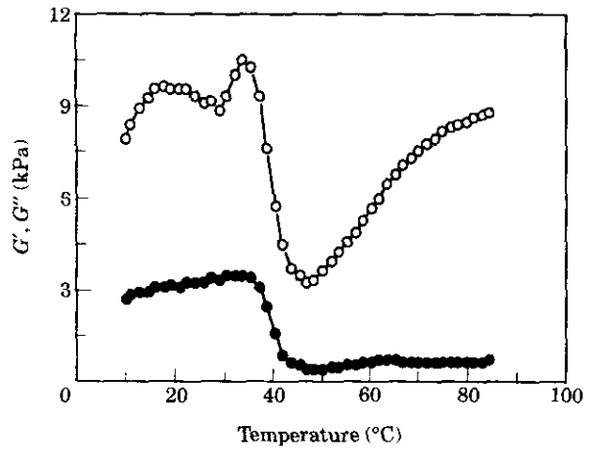

Fig. 2 Changes in storage modulus (G') (○) and loss modulus (G'') (●) for surimi sol during heating

ticity measurement and rotational viscometric/TSRM measurements. The results of our study indicate that the rotational cylindrical viscometry can be useful for continuous monitoring of viscosity changes during thermally-induced sol–gel transition with a simple setup required.

Viscosity thermogram

As shown in **Fig. 1** (heating rate 2.2 °C/min), there was a decrease in viscosity up to 36 °C, followed by a rapid increase, reaching a peak at around 40 °C. According to Montejano *et al.* (12), such thermally-induced rheological changes may be associated with a setting phenomenon. The abrupt increase in viscosity of fish actomyosin solutions above the 30–36 °C temperature range was observed by other workers (13–15). They attributed the increase in viscosity to the entanglement of partially unfolded actomyosin molecules. Immediately after the peak, there was a rapid decrease in the viscosity up to 60 °C for 2.2 °C/min and 50 °C for 0.5 °C/min. A predominant transition occurred at 40 °C at all heating rates with the sharpest at 2.2 °C/min. A similar result was observed in the TSRM thermogram (5) when a croaker surimi was tested at 1.0 °C/min. The decrease in the viscosity at around 60 °C was probably due to sol–gel transformation where the viscosity dropped before it rose as the protein sol started to aggregate into network formation with water release due to thermal syneresis. On the other hand, the increase in the viscosity above 60 °C appeared to be a result of transition from a loose network to a compact network formation in which the material was no longer in a sol state for viscosity measurement.

Effect of ingredients on viscosity in the composite surimi sols during heating

The characteristic viscosity thermograms of the surimi sols containing different types of ingredients are presented in **Figs 3–6**, where **Fig. 3** shows a thermogram of egg albumin-incorporated surimi sol. Addition of egg albumin did not shift the transition peak at 40 °C, but decreased the apparent viscosity almost proportionately as its level increased (**Fig. 7**). Such reduction of viscosity after addition of egg albumin may be due to reduced continuity of the surimi sol matrix and egg albumin being less viscous.

Addition of starch also decreased the apparent viscosity as

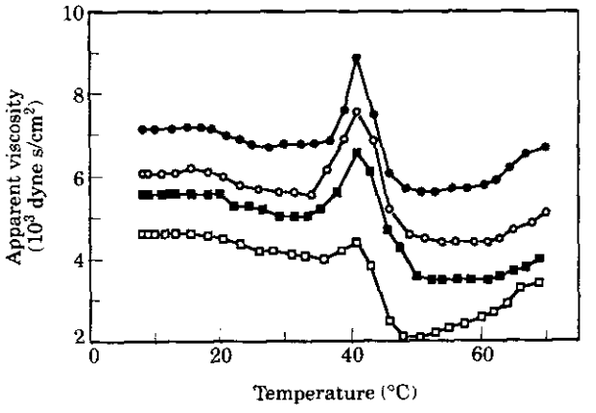

Fig. 3 Viscosity changes in egg albumin-incorporated surimi sols during heating. (●) control; (○) 10 g/kg; (■) 20 g/kg; (□) 30 g/kg

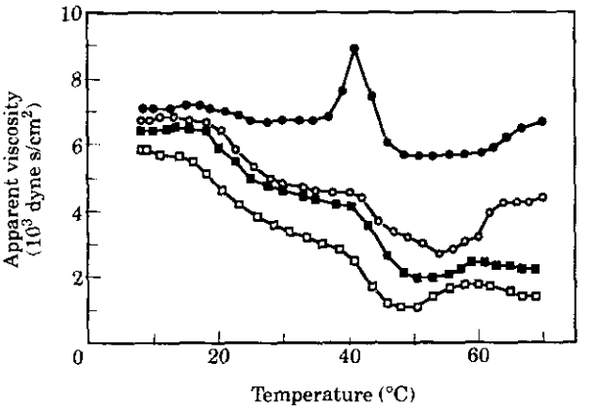

Fig. 4 Viscosity changes in starch-incorporated surimi sols during heating. (●) control; (○) 40 g/kg; (■) 60 g/kg; (□) 80 g/kg

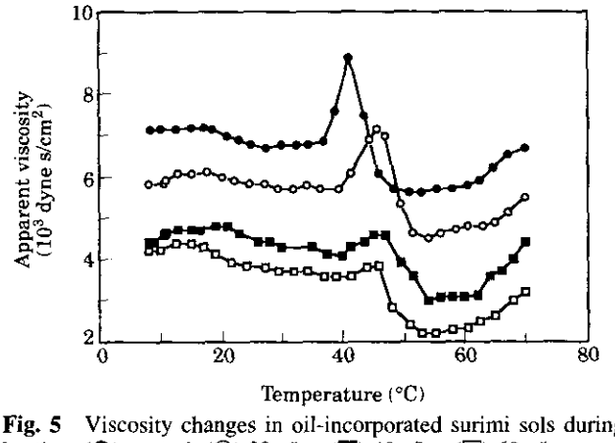

Fig. 5 Viscosity changes in oil-incorporated surimi sols during heating. (●) control; (○) 20 g/kg; (■) 40 g/kg; (□) 60 g/kg

seen in egg albumin-incorporated surimi sols (**Fig. 4**). However, no apparent transition peak was observed at all starch levels, although 40 and 60 g/kg levels showed slight transitions at 40 °C. The transition peak gradually disappeared as the starch level increased. The disappearance of transition peak with addition of starch may be explained by interfered protein aggregation. The occurrence of secondary transition at around 50 °C, which peaked at around 60 °C, coincided with the onset of gelatinization of aqueous starch at around 63 °C (**Fig. 8**). The heights of the transition peaks at 40 °C were a function of the concentration of surimi (**Fig. 7**).

Addition of oil increased the transition temperature from 40

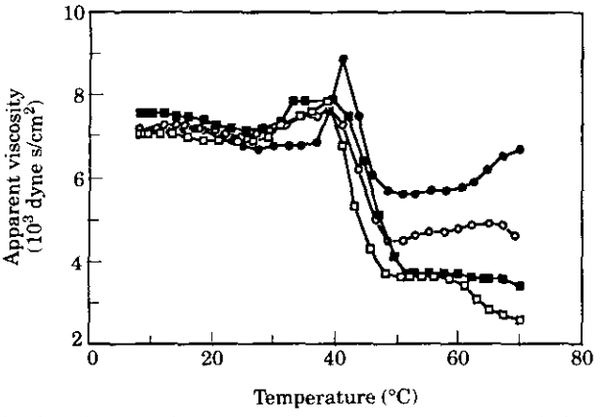

Fig. 6 Viscosity changes in carrageenan-incorporated surimi sols during heating. (●) control; (○) 2 g/kg; (■) 4 g/kg; (□) 6 g/kg

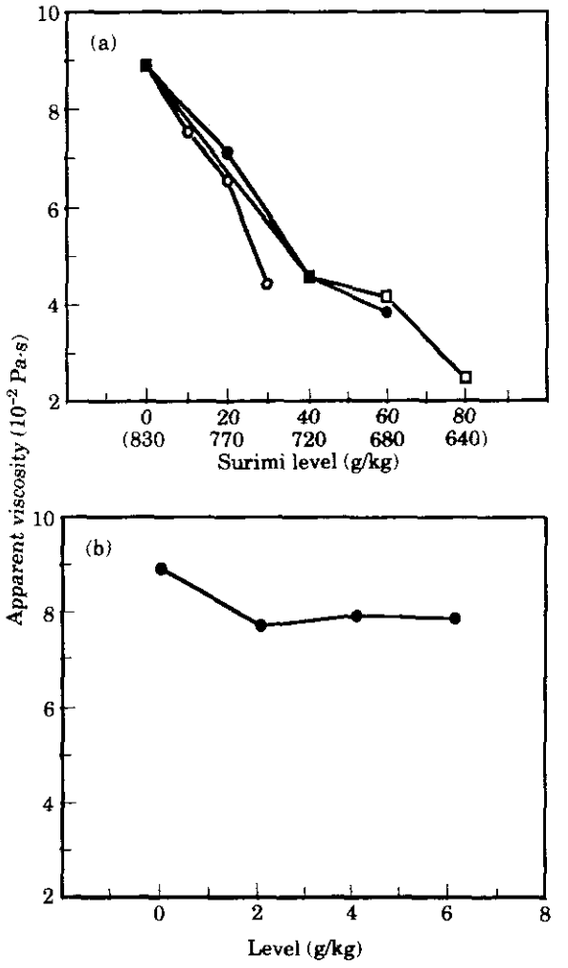

Fig. 7 Viscosity of transition peaks near 40 °C in surimi sols in the composite system. (a) (○) egg albumin; (□) starch; (●) oil; (b) (●) carrageenan

to 47 °C and decreased the apparent viscosity (**Fig. 5**). Similarly to egg albumin and starch, the extent of reduction in the height of the transition peak appeared to be in a linear function of the level of oil (**Fig. 7**). The decreased viscosity of oil-incorporated surimi sol may be explained by the lubrication effect of oil and a reduced continuity of the surimi sol. The delayed transition after addition of oil might have been caused by physical interference of oil with thermally-induced gel network formation.

In **Fig. 6**, the carrageenan-incorporated surimi sols showed higher viscosity than the control in the temperature range up to 38 °C with no apparent transition peak. This indicates that carrageenan appeared to have a thickening effect in the low temperature range (below 40 °C) and might have hindered a formation of cohesive protein network as the sol reached the transition point. The thickening effect of carrageenan in the surimi sol resulted from its water absorption and consequent swelling of the dispersed colloid (16). Fennema (17) and Glicksman (18) suggested that the carrageenan anion reacts with protein to form a protein–carrageenan complex that can exist as a stable dispersion and increase viscosity. The temperature for subsequent drop and leveling off in the viscosity of sol (**Fig. 6**) coincided with that for activation of aqueous carrageenan as indicated by an increase in the viscosity (**Fig. 8**). This finding suggests the important role of water in viscosity development as the viscosity is affected by a moisture shift during activation of carrageenan. The occurrence of transition at a lower temperature with addition of carrageenan may be related to the onset temperature for an activation of carrageenan at around 35 °C (**Fig. 8**) compared with that of surimi sol (40 °C). Unlike other ingredients, no significant variations in viscosity and temperature were observed at the transition peak irrespec-

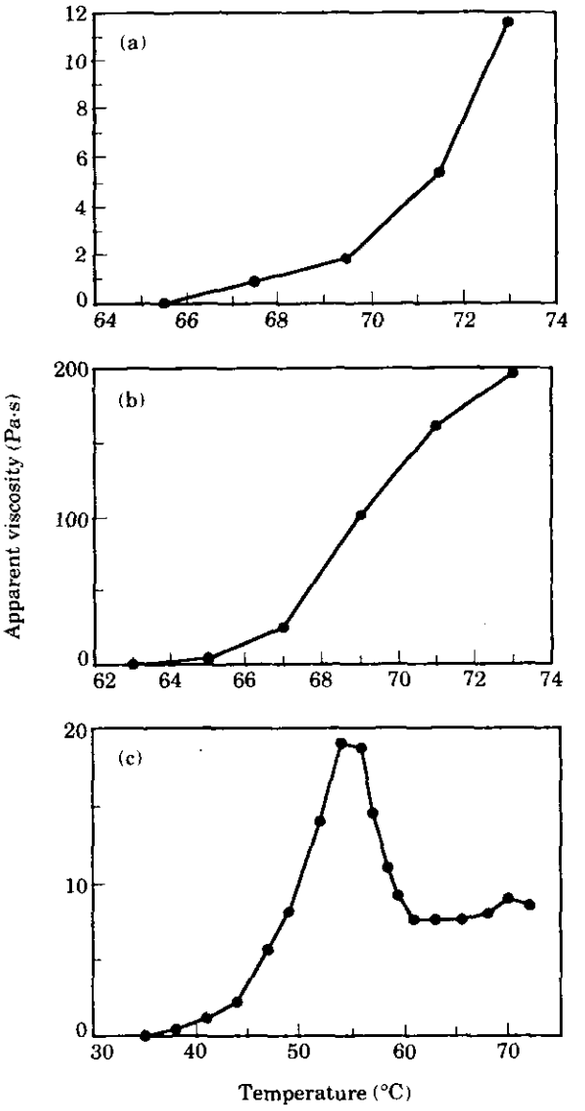

Fig. 8 Changes in viscosity of (a) 100 g/kg egg albumin (b) 100 g/kg starch and (c) 40 g/kg carrageenan slurries during heating to 75 °C

tive of the levels of carrageenan. However, beyond the transition temperature the changes in viscosity were affected by the level of carrageenan added. The lack of occurrence of apparent transition peaks in both starch and carrageenan can be explained by a hindered viscosity development as a result of protein–starch/carrageenan interaction.

The rotational cylindrical viscometry appeared to be a simple and yet sensitive method for continuous monitoring of the viscosity changes in sol–gel transition.

Conclusions

Rotational cylindrical viscometry is a simple and yet sensitive method for monitoring the viscosity changes in the composite surimi sols during heating in the temperature ranging from 5 to 60 °C. The sol–gel transition was initiated by an early transition at around 40 °C, followed by a subsequent transition at around 70 °C with completion of a network formation. The addition of ingredients not only reduced the viscosity and the height of the transition peak, but also shifted the transition peaks. Such reduction of viscosity was probably due to interference with protein hydration and network formation as well as dilution effect except for carrageenan which showed a thickening effect in the low temperature range below 40 °C. The pattern of such thermally induced viscosity changes at transition was greatly influenced by the type and level of ingredients. Egg albumin appeared to be assimilated into surimi protein, maintaining the same transition temperature as the surimi protein, while starch and carrageenan competed for water with surimi protein, thus hindering hydration and cohesive network formation as they were thermally activated. Oil, on the other hand, was neutral and physically interfered with network formation, resulting in delayed transition with slightly reduced transition peak height.

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