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TEXTURAL PROPERTIES AND STRUCTURE OF STARCH-REINFORCED SURIMI GELS AS AFFECTED BY HEAT-SETTING

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Abstract

The gel forming behavior of red hake (Urophycis chuss) surimi with and without starch and its relationship to the structure of the gel matrix were studied. For surimi gels without starch, a combination of preheat-setting at 40 C and cooking at 90 C resulted in significantly greater gel strength than cooking alone. However, preheat-setting of gels containing wheat or potato starch had no significant effect on gel strength demonstrating an opposite trend in gel strength due to the differences in swelling power, water holding ability and gelatinization temperature between potato and wheat starches. This difference in gel forming behavior due to the sources of starch and heat-setting prior to cooking correlated with changes in the structure of the matrix as evidenced by the results of image analysis. An examination of the microstructure of the gel matrix by light and electron microscopy showed that the structural differences may be due to the different protein matrix density as reflected in the increased gel strength.

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KEY WORDS: Starch in surimi gel structure, wheat, potato, rheology, texture.

Introduction

Surimi is a Japanese term for mechanically deboned fish flesh which has been washed with water and mixed with cryoprotectants for a good frozen shelf life. It is used as an intermediate product for a variety of fabricated seafoods. Due to its high functionality, surimi can be substituted for a variety of traditional animal and vegetable proteins (Lee, 1984).

It has been reported that heat-setting at 40-50 C prior to cooking at 90 C resulted in a stronger gel than cooking alone (Okada, 1959a,b). Recently Wu and his coworkers (1985a) examined physical changes in a surimi-starch system during thermal processing by monitoring starch gelatinization and protein denaturation with a differential scanning calorimeter. They found that gelatinization temperature, degree of swelling and water uptake of starch granules influenced the textural properties of a cooked gel, and the addition of starch resulted in higher failure stress but no significant effect on failure strain.

Composite gel-reinforcing effect of starch has been suggested by several workers (Okada and Yamazaki, 1957; Wu et al., 1985b). Little is known, however, about the effect of cooking methods and ingredients on textural properties with respect to the microstructure of gels. This prompted us to investigate the gel forming behavior of surimi as affected by cooking methods and type of starch, with the focus on gel microstructure and its relationship to gel textural properties.

Materials and Methods

Preparation of surimi

Red hake (Urophycis chuss) caught off Galilee, Rhode Island was processed into surimi within 24 hours. Fresh red hake fillets were run through a deboner (Model 694, Baader North America, New Bedford, MA) with a drum having 5 mm diameter perforations and washed 3 times using 1 part fish meat to 4 parts water (w/w). Each washing was carried out at a water temperature of 10 C for 10 min and was followed by draining in a rotary rinser prior to the subsequent washing. The resulting slurry from the rinser was passed through a strainer (Model Bibun SUM 420, Ryan Engineering, Seattle, WA) to remove any residual dark connective tissue, black skin, bone and scale. The strained meat was then run through a screw dehydrator (Model Bibun SR 1000, Ryan Engineering, Seattle, WA) to remove

TABLE 1 - Types of surimi gels prepared

Types	Types of starch	Cooking methods used
I	Surimi paste without starch	cooked at 90 C for 40 min in a water bath and immediately cooled in running tap water for 20 min
II	Surimi paste without starch	heat-set at 40 C for 30 min and then treated in the same manner as Type I
III	Surimi paste with wheat starch	treated in the same manner as Type I
IV	Surimi paste with wheat starch	treated in the same manner as Type II
V	Surimi paste with potato starch	treated in the same manner as Type I
VI	Surimi paste with potato starch	treated in the same manner as Type II

water; chopped with sugar, sorbitol and sodium tripolyphosphate at 4%, 4% and 0.2%, respectively, in a 50 lb-capacity silent cutter (Model VCM 40, Hobart Manufacturing Company, Troy, Ohio) at a low speed (1,750 rpm) for 30 sec; and subsequently vacuum-packed (Model GK 120, Smith Equipment Co., Clifton, NJ) in cryobags to be stored at -20 C until used.

Preparation of heat-induced surimi gel

The thawed surimi (overnight in a refrigerator, -2 + 0.5 C, 78% moisture) was chopped with 2.5% salt (Morton plain salt, Morton Thiokol, Inc., Chicago, IL) in a silent cutter for 9 min. This was followed by additional chopping for 3 min with or without 5% wheat or potato starch and enough ice-chilled water to adjust the moisture level to 78%. The quantities of salt and starch added were based on a surimi weight basis. The chopped surimi paste was stuffed into 30 mm diameter cellulose casings and cooked. Six types of samples were prepared due to different cooking methods and types of starches incorporated as shown in Table 1. Wheat starch (Aytex P) and potato starch were obtained from Henkel Corporation (Minneapolis, MN) and Colby Starch Company (Caribou, ME), respectively.

Measurement of textural properties

The prepared gels were left overnight at room temperature to equilibrate to room temperature and were cut into cylindrical shapes (30 mm diameter and 25 mm long). Following the procedures proposed by Lee (1984) and using an Instron testing machine (Model 1122, Instron Engineering Corp., Canton, MA), compressive force, expressible moisture, compressive energy and penetration force were measured. Compression was done uniaxially at a crosshead speed and a chart speed of 50 and 100 mm/min, respectively, without having the specimen lubricated.

Compressive force with failure at 90% deformation was used as an index of the cohesiveness of the gel. The 90% deformation was sufficient to cause all samples tested in this study to rupture. At the same time, the amount of moisture expressed upon compression was measured by collecting the fluid on filter paper and recorded in terms of % expressible moisture on a sample moisture weight basis. The compressive energy (area of 2nd and 3rd compression peaks, Kg-mm) was measured as an index of chewiness during three repeated compressions at 90% deformation using a 10 cm dia compression head. Penetration force at 90% deformation was measured as an index of rigidity by using a plunger of 9.5 mm diameter.

Light microscopic study

For examination of surimi gels with a light microscope, small gel blocks (0.5 cm cubes) were frozen in liquid nitrogen and sectioned into 10-12 μm with a cryomicrotome (Model 3398, Damon/IEC Division, Needham Hts., MA). Prepared sections were mounted on slides by touching the sections with a slide at room temperature. In this manner, the cold sections freely adhered to the surface of the slide. They were then dehydrated by first dipping the specimen in 50% ethanol for 5 min and then in 70% ethanol for 5 min. The protein was stained with 0.1% Eosin Y in 70% ethanol (Humason, 1967) for 10 min. and the excess stain was rinsed off first with 70%, then with 50% ethanol and finally with water. Starch was stained by transferring the specimen while wet with water into the iodine staining dish containing finely ground iodine crystals and anhydrous $CaSO_4$, covered with a watch glass. Iodine vapor method was based on that used by Little (1957). When thoroughly dry, the slide was placed in xylene for 5 min and mounted in Cytoseal (Thomas Scientific, Swedesboro, NJ). The prepared specimens were examined with an Olympus microscope (Model CHBS, Olympus Optical Co., LTD., Japan).

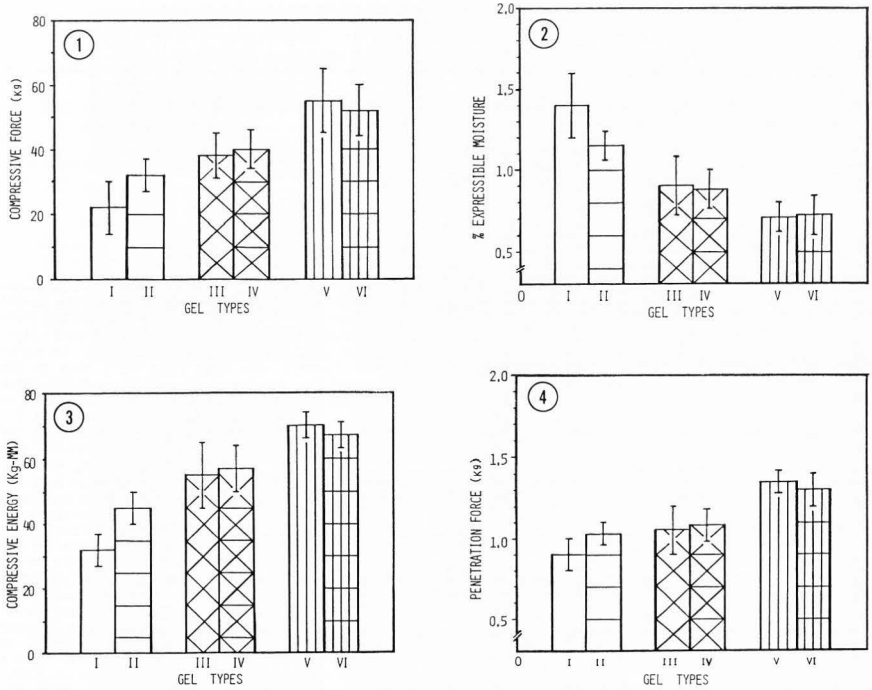
For examination of starch gel, 15% potato starch slurry in distilled water (W/V) was cooked at 90 C for 40 min and placed at room temperature overnight and prepared in the same manner as surimi gels for a light microscopic study.

Image Analysis

A Hipad Digitizer (Houston Instrument, Austin, TX) connected to an IBM computer (Model 5160, IBM computer Inc., Armonk, NY) was used to measure volume fractions of starch granules in fish protein before and after cooking. The average area of the field examined was 0.25 mm^2. The result is an average of 3 replica.

Electron Microscopic Study

Small gel blocks (0.5-1.0mm) were fixed in 2% osmium tetroxide and 0.8% potassium ferricyanide (McDonald, 1984) in 0.1 M TRIS buffer (pH 7.2) for 4 hours at room temperature. The specimens were then block stained with 1% uranyl acetate and 1% DMSO in distilled water for 2 hours at room temperature, dehydrated in a series of increasing ethanol concentrations, infiltrated with propylene



Figures 1 to 4. Effects of 5% starch and heat-setting on - **(Figure 1)** Compressive force of surimi gel; **(Figure 2)** percentage expressible moisture of surimi gel; **(Figure 3)** compressive energy of surimi gel; and **(Figure 4)** on penetration force of surimi gel.

oxide and embedded in Araldite 506 mixture (Luft, 1961). Sections of 60-90 nm thickness were mounted on carbon grids previously coated with parlodion, and stained with 2% uranyl acetate in 50% ethanol for 30 min. They were then treated with Reynold's lead citrate solution (Reynold, 1963) for 5 min., and rinsed with 0.02 N NaOH and with distilled water. The prepared specimens were examined with a JEOL 1200-EX electron microscope at 80 kV.

Statistical Analysis

Analysis of variance performed by the Statistical Analysis System (SAS, 1982) was used to determine differences in the physical properties among surimi gels due to different cooking methods and types of starches incorporated. Duncan's multiple range test (Duncan, 1955) was performed to determine the significance of the mean separation at 5% significance level.

Results and Discussion

Gel strengthening ability varies from starch to starch (Kim and Lee, 1987). In this experiment potato and wheat starches were used because they are most commonly used in commercial products. The textural properties, compressive force, % expressible moisture, compressive energy and penetration force of six different surimi gels are shown in Figs. 1 - 4, respectively.

Gels prepared with heat-setting (Type II) exhibited significantly ($P<0.01$) higher compressive force, water holding ability (lower % expressible moisture) and penetration force than those prepared without heat-setting (Type I) when starch was not incorporated. The structure of a protein gel matrix of Type II (Fig. 5b) was more uniform than that of Type I (Fig. 5a). Many areas of aggregated material were observed throughout the latter protein gel (Type I). These observed structural differences in the protein gels were reflected by the differences in gel strength (Figs. 1, 3 and 4) and water holding ability (Fig. 2).

Trends for all textural parameters of the gels prepared with wheat starch were similar to those of the gels prepared without starch, with no significant difference between the gels prepared with (Type IV)

TABLE 2 - Size of starch granules before and aftercooking of surimi paste

Types of starch incorporated	before cooking	After cooking: without heat-setting	After cooking: with heat-setting
wheat	0.29 ± 0.01	3.06 ± 0.24	4.50 ± 0.36
potato	2.24 ± 0.15	16.21 ± 2.85	10.69 ± 1.26

Values are mean volume ± S.D. of starch granules in $mm^3 \times 10^{-5}$

and without (Type III) heat-setting prior to cooking (Figs. 1 - 4). However, the gels prepared with potato starch showed an opposite trend in which the gel strength with heat-setting was lower than the one without heat-setting. But no significant difference was found between Type V and VI gels ($P < 0.05$). This may be explained by the fact that: 1) The fish protein starts to set at 40 C, which is substantially lower than the gelatinization temperature of potato starch, which ranges from 56 to 66 C (Leach, 1965) ; 2) The preset protein gel matrix prior to starch gelatinization could restrict the swelling of the starch granules during cooking. Water binding in the protein gel reduced the availability of water for the gelatinization of potato starch more in the protein gel cooked with (Type VI) than that cooked without (Type V) preheat-setting. The above reasoning explains why the gelatinized potato starch granules in the Type VI gel were slightly smaller than those in the Type V gel (Table 1). Accordingly, the Type VI gel had a slightly lower gel strength than did the Type V gel (Figs. 1 - 4). In contrast, the swelling power, water holding ability and solubility of wheat starch are much lower than those of potato starch (Leach, 1965). Therefore, the gelatinization of wheat starch during preheat-setting was not affected as much as that of potato starch by the amount of moisture held in the protein gel matrix. This was evidenced by the fact that the gelatinized wheat starch granules in the Type IV gel were slightly larger than those in the Type III gel. This also reflected the difference in gel strength between the Type III and Type IV gels, where the Type IV gel showed a slightly higher gel strength than the Type III gel. As mentioned above, the swelling power of starch plays an important role in the strengthening of a surimi gel. Wheat starch granules expanded an average of 10.5 times (average volume increase: 2.8 $mm^3 \times 10^{-5}$) after cooking without heat-setting, and an average 15.5 times (average volume increase: 4.2 $mm^3 \times 10^{-5}$) after cooking with heat-setting (Table 2). In contrast, potato starch granules expanded an average of 7.2 times (average volume increase: 14.0 $mm^3 \times 10^{-5}$) after cooking without heat-setting, and an average of 5 times (average volume increase: 8.5 $mm^3 \times 10^{-5}$) after cooking with heat-setting. This indicates that potato starch had a greater swelling power than wheat starch and explains the greater gel strengthening ability of potato starch (Figs. 1 - 4).

Before cooking, the compact amylose and amylopectin fractions in the intact wheat (Fig. 6a) and potato (Fig. 7a) starch granules in the surimi paste were dark blue-black and demonstrated their characteristic birefringence in polarized light (Figs. 6b and 7b). After cooking, the loosely arranged amylose fraction was light blue-black due to the swelling of the starch granules, while a small portion of the intact amylose fraction was dark blue-black in Figs. 8a, 8b, 9a and 9b (The red background is fish protein gel stained by Eosin Y). Based on the studies reported by Yamaguchi et al. (1979), and Christianson et al. (1982), most of amylopectin was assumed to remain in the gelatinized starch at the temperature used for cooking in this experiment. According to Rundle et al. (1944), the amylopectin forms an unstable red-purple complex with iodine. However, the complex is not seen in these figures because the amylose fraction stained by iodine covers the red amylopectin-iodine complex. Figs. 8 and 9 show that gelatinization of starch in starch-fish protein system is restricted due to the limited water, resulting from the competition of water between starch and protein systems during cooking. In contrast, starch granules in starch-water system cooked at 90 C for 40 min lost their shape completely and fused and adhered to one another (Fig. 10).

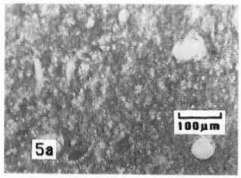
Figure 5. Surimi gel prepared without starch. (a) Cooked at 90 C for 40 min (Type I); (b) Prepared with heat-setting at 40 C for 30 min prior to cooking in the same manner as Type I (Type II).

Figure 6. Surimi paste with 5% wheat starch. ST: starch granules; FP: fish protein gel. (a) Before cooking; (b) same as Fig. 6a but photographed in polarized light.

Figure 7. Surimi paste prepared with 5% potato starch. ST: starch granules; FP: fish protein. (a) Before cooking; (b) same as Fig. 7a but photographed in polarized light.

Figure 8. Surimi gel prepared with 5% wheat starch. IA: intact amylose; FP: fish protein. (a) Cooked in the same manner as Type I (Type III); (b) cooked in the same manner as Type II (Type IV).

Figure 9. Surimi gel prepared with 5% potato starch. IA: intact amylose fraction; FP: fish protein. (a) Cooked in the same manner as Type I (Type V); (b) cooked in the same manner as Type II (Type VI).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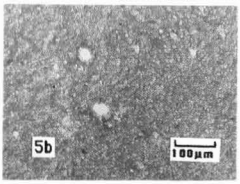
5a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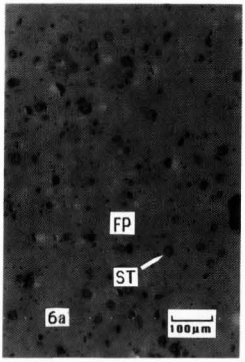
FP
ST
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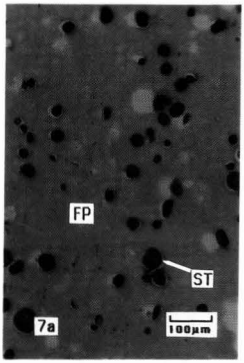
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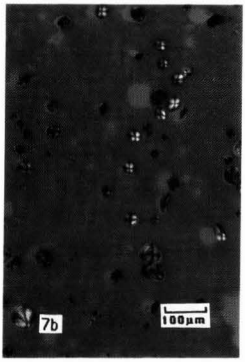
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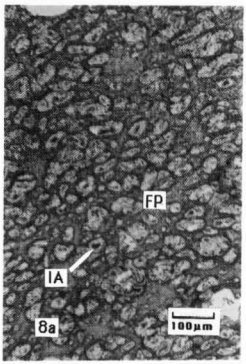
FP
IA
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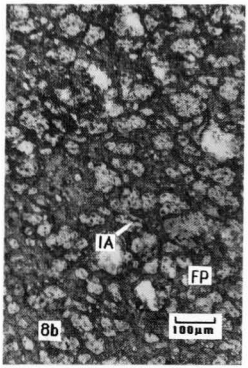
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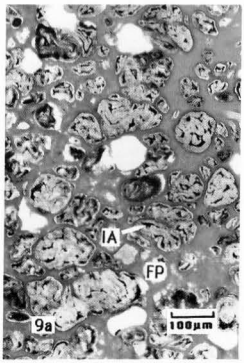
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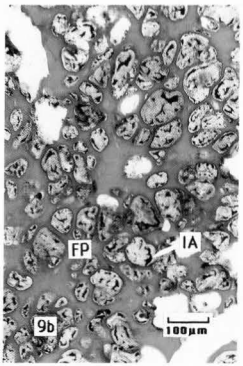
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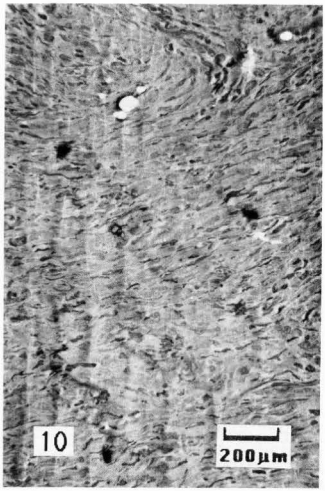
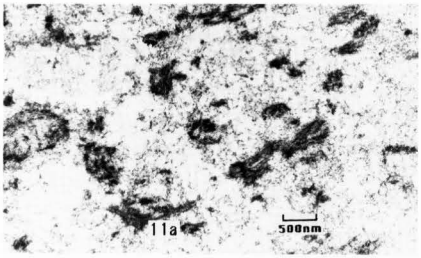


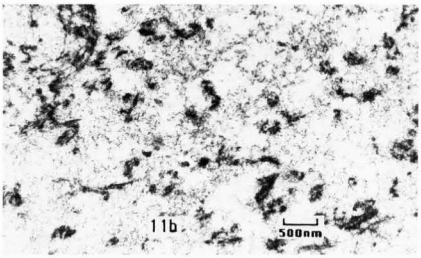
Figure 10. Potato starch gel (15% potato starch suspended in distilled water, W/V, was cooked at 90 C for 40 min and placed at room temperature overnight before the preparation in the same manner as for surimi gels for light microscopic study

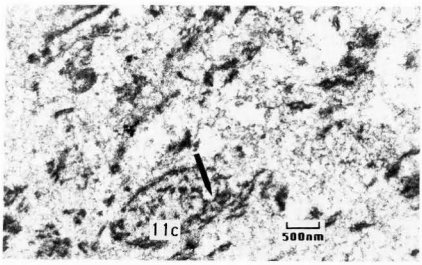
Figure 11. Transmission electron micrographs of surimi gel. (a) Surimi Type I gel; (b) Surimi Type II gel; (c) Surimi Type III gel; (d) Surimi Type V gel.

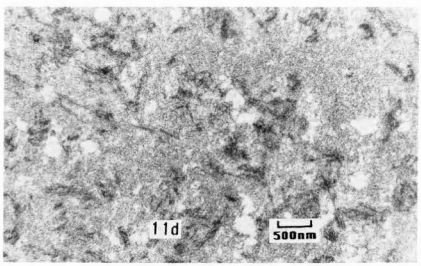
The same result was previously observed after cooking at 80 C for 75 min. using a scanning electron microscope (Christianson et al., 1982).

The textural properties of gels determined by an Instron testing machine and the gross microstructure observed by light microscopy correlated with the fine microstructure of the gel examined by transmission electron microscopy. The following explanation for the composite reinforcing mechanism of starch in surimi gels has been proposed. The starch granules embedded in the protein gel absorb water from the matrix and push the matrix as they swell during cooking, and cause it to become more compact. This process has been visualized in the electron micrographs (Figs. 11a - 11d). The fine structure of surimi gels studied by a transmission electron microscope clarified the network structure which is composed of myofilaments and other protein components in myofibrils, and correlated gel strength with the network structure. The matrix with network structures of single myofilament and bundles of irregularly arranged filaments are seen to be random-









ly dispersed in all figures. Collagen-like dark objects (arrow) are illustrated in Fig. 11c. Some correlation was found between the microstructure profiles and gel strength. Gel strength increased with increased uniformity of the dispersed phase in the gel. This result was consistent with previous reports (Miyake, 1965; Miyake et al., 1971; Sato et al., 1984).

There seemed to be no significant difference in the uniformity of the dispersed phase between Type I (Fig. 11a) and Type II (Fig. 11b) gels. The differences in gel strength and water holding ability between these two gel types (Figs. 1 - 4) were attributed to the uniformity of the protein gel as mentioned earlier (Figs. 5a and 5b). The gel prepared with potato starch (Type V) (Fig. 11d) had a more uniform matrix distribution of the randomly dispersed phase than the gel prepared with wheat starch (Type III) (Fig. 11c). This resulted from the fact that potato starch increased in volume more than wheat starch (Table 2). In other words, potato starch produced less agglomerated protein gel matrix, and accordingly, a greater gel strength and water holding ability (Figs. 1 - 4) than wheat starch. Both starch-incorporated gels (Type III and V) had noticeably higher densities of the dispersed phase, which resulted in greater gel strength than the gels prepared without starch (Type I and II). Therefore, it can be concluded from these results that the presence or absence of starch and the type of starch clearly influence the density of the gel matrix and the gel strength.

Acknowledgements

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Discussion with Reviewers

E.B. Bagley: What is the swelling power you refer to?

Authors: The term swelling power in this paper is neither the degree of hydration nor a rate measure of swelling of the starch granules. It is an index of the increased volume during cooking.

D.D. Christianson: Can you clarify the compression force measurement at 90% deformation in relation to cohesiveness? What if the specimen does not rupture at 90% deformation? What if it ruptures at 30%? What if it does not rupture at all?

Authors: The measurement was made essentially to determine compressive force which results in failure or rupture of the specimen. In our experiment, all gel specimens that we tested ruptured before 90% deformation. Here 90% means that the instrument was set up to compress a specimen uniaxially to 90%. Previously, we observed that some low-moisture gels did not fail at 90% and required 95% deformation.

As the procedure says, we measured a force at failure regardless of the deformation applied. If the rupture occurred at 30%, we would simply measure the force corresponding to 30% deformation as a compressive force. Cohesiveness may be more correctly defined as the extent of deformation at failure, namely, a strain at failure. From our analysis of data, however, the strain at failure was not as discriminative as compressive force. Therefore, we decided to measure the compressive force at failure as an index of cohesiveness.

E.A. Davis: What criteria do the authors use to conclude that Fig. 11c was less dense than Fig. 11d?
Authors: Increased volume of potato starch was much greater than that of wheat starch resulting in greater decrease in the volume of gel matrix. This causes the gel prepared with potato starch to become more compact and consequently, to become less agglomerated and more uniform distribution of the dispersed phase.

D.P. Dylewski: What effect does preparing the various gels for TEM analysis (e.g., hydration, fixation, dehydration, ETOH) have on the density of the gel matrix?
Authors: Fish protein examined in this study has been solubilized while chopping with 2.5% salt and denatured by cooking (i.e., fixed). Therefore, little change in dimensions of protein gel matrix can be expected during dehydration with increasing concentrations of ethanol in the preparation. The protein gel was infiltrated with a liquid Araldite mixture embedding medium and polymerized to produce a solid plastic block. This block was, then, cut into thin sections. Therefore, the density of the gel matrix in the sections are not affected by hydration during staining.

T.C. Lanier: How can you be sure that an amylopectin-iodine complex has formed, if you cannot see it?
Authors: It has been reported that iodine molecules form a complex with amylose and amylopectin in a parallel orientation within the interior polar field of the helix of starch molecule: a stable blue complex with amylose and the less stable, red complex with amylopectin due to the short length of the branches. This unstable red complex was covered by the blue complex and cannot be seen in this preparation.

T.C. Lanier: What is the "dispersed phase" you refer to?
Authors: Preparation of surimi and heat-induced surimi gel involves a vigorous chopping process. Consequently, most of the myofilaments are chopped and fragmented, and dispersed in the gel.