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The objective of this study was to investigate effects of starch on rheological, microstructural, and color properties of surimi-starch gels. Native and modified starches with different ratio of amylose and amylopectin were evaluated with pollock surimi to determine their behavior in surimi-starch gels. According to large strain fracture results, it was demonstrated that the effect of starch on the texture of surimi-starch gels depended on the concentration and modification method of starch as well as the ratio of amylose and amylopectin. The lower starch concentration (3%) increased the gel strength more effectively than the higher starch concentration (6% or 9%). Modification facilitated the granule to swell easily and resulted in increased shear stress. The more amylopectin in starch, the stronger surimi-starch gel. Conversely the more amylose, the weaker the gel. The influence of heating temperature on the texture depended on gelatinization temperature of individual starches. A longer heating time slightly increased shear stress of surimi-starch gels. Shear strain was not affected by heating time and temperature. The larger granules of the starch resulted in the stronger gel. The color (lightness and

yellowness) of surimi-starch gels also depended on the concentration and the properties of starch. The more the granule swelled, the lower the L* value and the lower the b* value of gels.

Non-fracture (stress relaxation) test was applied to measure the effect of the starch on the viscoelastic properties of surimi-starch gels. Once three dimensional network structure of myofibrillar proteins was formed, additional thermal treatments did not influence the viscoelastic properties of surimi gels. When starch was added into surimi, the viscoelastic properties of surimi-starch gels were changed by the type and concentration of starch. All gels showed a typical behavior of viscoelastic solid due to a dominant role of covalent bonds and reinforcement of starch granules in surimi-starch gels.

Effects of Starch on Rheological, Microstructural, and Color Properties of Surimi-Starch Gels

by

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Dean of Graduate School

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Hong Yang, Author

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CONTRIBUTION OF AUTHORS

Dr. Jae W. Park was involved in the experimental design, analysis and preparing the manuscript. Dr. Sakharam Patil was involoved in the experimental design in one of three studyies (attached in the appendix).

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EFFECTS OF STARCH ON RHEOLOGICAL, MICROSTRUCTURAL, AND COLOR PROPERTIES OF SURIMI-STARCH GELS

Chapter 1 Introduction

Surimi, made from inexpensive and abundant fish, such as, Alaska pollock and Pacific whiting, has been successfully used for a high quality surimi seafood product. Before 1960, surimi could just be kept in a refrigerated condition and should be used within a few days because freeze-induced denaturation caused poor functionality. When low molecular carbohydrates such as sucrose, was added into surimi before freezing, the denaturation of fish muscle protein was greatly inhibited (Nishiya et al., 1960). Since then, the production of surimi rapidly increased, because the industry did not have to depend on refrigerated surimi. Over the last 5 years, the United States has produced more than 40% of the world surimi, about 150,000 to 190,000 metric tons a year (Park, 1995a).

The most important part of surimi is its myofibrillar protein. Its uniqueness is based on the ability to "set" into gels of high cohesiveness at low temperatures (0-40°C) and produce extremely strong gels upon final cooking (Hamann and MacDonald, 1992). Such gels show viscous and elastic properties, i.e. viscoelasticity. The torsion test has been commonly employed as a fundamental analytical method to measure the fracture property of surimi gel under large strain. Shear stress indicates gel strength and depends on protein concentration, processing condition, and ingredient function, while shear strain

indicates the function of protein quality as affected by denaturation (Hamann, 1988). Stress relaxation, which is a common method to determine the non-fracture (small strain) mechanical properties of solid-like foods (Peleg, 1979), reveals viscoelastic properties of the gel (Mohsenin, 1986). Microscopy is a unique method to evaluate food microstructure (Kaláb et al., 1995) facilitating its physical properties (Davis and Gordon, 1984; Kazemzadeh et al., 1982).

The structural integrity of surimi seafood is based on a continuous protein matrix with a significant contribution of starch. Several studies were conducted to investigate the effects of starch on the texture of the gel (Chung and Lee, 1991; Kim and Lee, 1987; Kim et al., 1987; Lee and Chung 1990; Lee and Kim, 1986a; Lee and Kim; 1986b; Lee et al., 1992; Ma et al., 1996; Okada, 1986; Park, 1995b; Park et al., 1997; Wu et al., 1985a; and Wu et al., 1985b.). During surimi seafood manufacturing, chopping can easily disperse starch particles. Its functional properties are rendered by heating, which causes the granules to swell, absorb water, and impart viscosity (Sanderson, 1996). When starch is added in the surimi seafood, it can modify texture, improve freeze-thaw stability, and decrease the cost while the texture of products is seldom changed (Lee et al., 1992; Park et al., 1997; Wu et al., 1985a). Most of the above research focused on the effect of starch content on texture or the effect of modified starch on freeze/thaw. The functionality of starch comes from the granule, which consists of two chemical components (amylose and amylopectin) and contains two physical phases (amorphous and crystalline) in the structure (Wang et al., 1989). During thermal processing or gelatinization, the change of these

properties of the granule will result in the change of the texture of food. These changes depend on the moisture content and the processing conditions, such as heating temperature and time. Pasteurization of imitation crab is more than 40 min. Few studies have reported how amylose, amylopectin or modification influence both the texture, the viscoelasticity, and the color of surimi seafood, and how heating temperature and time affect the texture, the viscoelasticity, and the color.

The objectives of this study were to evaluate the mechanical behaviors of surimi-starch gels: large strain fracture by using torsion test, small strain non-fracture by using stress relaxation test, microstructure by light microscopy, and the color. The outcome of this study could facilitate the better understanding of effects of starch properties and thermal processing conditions (temperature and time) on texture, viscoelasticity, microstructure and color of surimi-starch gels.

Chapter 2 Literature Review

Surimi and gelation

Surimi is stabilized fish myofibrillar proteins manufactured through a series of continuous processing steps including heading, gutting, filleting, deboning, washing, dewatering, blending with cryoprotectants, and freezing (Lee, 1984; Toyoda et al., 1992). The fish muscle proteins can be categorized into three groups according to their solubility: sarcoplasmic proteins which are soluble in water; myofibrillar proteins which are not soluble in water or dilute salt solution but all are soluble in salt solutions of high ionic strength; and stroma proteins which are not soluble in acid, alkaline, or salt solutions of high ionic strength (Hultin, 1985; Suzuki, 1981). Recent studies from Stefansson and Hultin (1994) as well as Lin and Park (1996) have demonstrated that myosin is highly soluble in water and very low ionic strength salt solution: the former from laboratory scale experiments and the latter from commercial surimi processing. Myofibrillar proteins, which cover 66-77% of the total proteins in fish muscle (Suzuki, 1981), are regarded as the most important component by surimi manufacturers because they can form the elastic gels upon thermal processing (Lanier, 1986; Lee, 1984). Sarcoplasmic proteins have poor gelation properties and sometimes inhibit the gelation of myofibrillar proteins. They can also deteriorate the texture because of the presence of heat-stable proteases which are activated in the temperature range (50°-70°C) (Shimizu et al., 1992). Stroma

proteins, which form connective tissue, are not water soluble. They have negligible effect on the texture of surimi product because fish muscle only contains a small part of stroma proteins (< 3-5%) (Lanier, 1996).

Myofibrillar proteins play a major functional role in production of surimi seafood and myosin is generally considered as the most effective protein in the gel. Myosin and actin, which are the two major myofibrillar proteins, can form actomyosin. Both myosin and actomyosin have a predominant role in surimi gelation, but the effect of actomyosin on gelation is originated from the myosin portion (Niwa, 1992). Among myofibrillar proteins, intermolecular salt linkages, which are formed between hydrophilic residues, are associated into an aggregate to protect those residues from water. When salt is added to surimi protein with a sufficient degree of comminution, it results in the rupture of salt linkages among myofibrillar proteins and increases their affinity for water. Thus myofibrillar proteins can be dissolved in the presence of salt during chopping. At the same time, salt also destabilizes the native structures of proteins prior to thermal denaturation (Park and Lanier, 1990).

According to Schmidt (1981), gelation is defined as protein association. Polymer-polymer and/or polymer-solvent interacts where attractive and repulsive forces are balanced. As a result, a well ordered tertiary network or matrix is formed. Gelation involves transition of a sol (polymer solution) to a gel (Aguilera, 1995). During thermal processing, myofibrillar proteins are initially denatured and then aggregated to form a

three dimensional, irreversible, and solid gel structure. Such gels provide a structural matrix and can hold water, flavor and other filling ingredients (Kinsella, 1976). The gel, formed from myosin, exhibits a high water-binding capacity and very strong elastic properties (Schmidt et al., 1981). Actin alone forms a very poor gel which can be strengthened when actin and myosin are mixed (Yasui et al., 1982).

There are four main types of bonds formed in surimi gel for supporting the network structure (Niwa, 1992): salt linkages, hydrogen bonds, hydrophobic interactions, and disulfide (covalent) bonds. Those bonds play a very important role in the stabilization of the network structure of surimi gels. Hydrogen bonds and hydrophobic interactions are more sensitive to temperature than disulfide bonds. In warm condition (about 50°C), hydrophobic interaction is increased and hydrogen bond is decreased; and in cool condition (about 5°C), hydrogen bond is enhanced (Howe et al., 1994; Park et al., 1997). The intermolecular salt linkage is formed among charged amino acids of the protein chain in the presence of salt (Niwa, 1992). Disulfide bond (330-380 kJ/mol) is not so easily broken like other bonds (8-84 kJ/mol) (Cheftel et al., 1985). Recently, role of non-disulfide covalent bonds induced by transglutaminase have been observed in the forming gels with preincubation at low temperatures (0° - 40°C) (An et al., 1996).

Starch and gelatinization

Starch is a polysaccharide consisting of numerous α-D-glucopyranosyl units in a linear and/or branched chains, i.e. a natural macropolymer of glucose, the major form in which carbohydrates are stored (Shannon and Garwood, 1984), and the most abundant in seeds, roots, and tubers (Whistler and Daniel, 1985). Of all polysaccharides, only starch has a small particle unit, granule (Whistler and Daniel, 1985). The starch granule is heterogeneous: chemically containing both amylose (linear) and amylopectin (branched), and physically containing both amorphous and crystalline phases (Biliaderis et al., 1986; Wang et al., 1989).

Amylose is a linear polymer of (1→4)-α-D-glucose, and its molecular weight is around 250,000 (1,500 anhydroglucose units); and amylopectin is a polymer of linear (1→4)-α-D-glucose chain branched by (1→6)-α linkage, and its molecular weight is around 10^8 (600,000 anhydroglucose units) (Blanshard, 1987; Hoseney, 1986). Under an iodine staining method, the blue color contributed by polyiodide ions is shown in the central core of the amylose helix (Hoseney, 1986). There is no definite separation between the crystalline and amorphous regions of starch granules (French, 1984). Amorphous region is about 70% of the starch granule and most of amylose is included in it; and crystalline region is composed of amylopectin (Blanshard, 1987). According to the x-ray scattering diffractograms, native starch can be categorized into three groups: A-type for cereal starches, such as maize, wheat and rice; B-type for tuber, fruit, and stem

starches such as potato, sago, banana starches; and C-type for intermediate starches between A and B-type, such as seed starches (French, 1984; Zobel, 1988).

Starch gelatinization and melting are the important phenomena occurring in various thermal processings of food operations because they provide unique textural and structural characteristics for the products. Starch granules are not soluble in cold water but can reversibly imbibe water and swell slightly upon excessive shear force (Whistler and Daniel, 1985). When starch granules are heated in suspension at a gelatinization temperature (usually about 60° - 70°C), the granules swell irreversibly many times to their original size (Miles et al., 1985). The swelling ability, which is directly relative to the texture of food, is influenced by heating temperature and time (Leach, 1965). Thus, heating temperature and time are two of the most important factors to influence the gelatinization characteristic of starch. Absorption of water is accompanied by the loss of order, the loss of crystallinity and the solubilization of amylose (Blanshard, 1987). At the same time, the viscosity of the suspension is dramatically increased and it becomes a hot paste. From microstructure, a fluid, composed of porous, gelatinized and swollen granules with an amylopectin skeleton, embedded in a hot amylose solution (Morris, 1990). Because those swollen granules are more susceptible to mechanical shearing, they can break down into fragments, microgels and molecules, resulting in the great decrease of the viscosity. They may also be autoclaved without shear force if they are held at higher temperature (> gelatinization temperature) for long time (1 hr) (Leach, 1965). When the

hot paste is cooled, the viscosity is increased. At the same time, starch molecules can reassociate, and retrogradation occurs, especially in linear chains associated with amylose.

For the food industry, various starches have been developed to stand high shear rate and shear force in processing equipment, the change of pH, high temperature (sterilizing process), and low temperature (storage) for a longer shelf life (Eliasson and Gudmundsson, 1996). However, the behavior of native starches in a certain application does not always satisfy different demands (Bohlin et al., 1986). Thus, physically and chemically modified starches have been developed to improve the functional properties of starch and contribute a myriad of applications to the industry. For example, potato starch granule is large so that it greatly increases the surimi gel strength. However, native potato starch in the surimi seafood can readily retrograde during the frozen storage. It results in the syneresis (water separation) and greatly deteriorates the quality of surimi seafood. If starch is modified by hydroxypropylation or acetylation with or without crosslinking, it can resist retrogradation (Lee et al., 1992). For chemical modification, substitution and cross-linking are commonly used. Some chemical components are induced into the starch granules as a substitute and modify the functional properties, such as phosphate (Whistler and Daniel, 1985; Wurzburg, 1986). The properties of modified starches, relative to the parent starches, change the viscosity of hot paste, gel strength, gelatinization temperature, dispersibility, and cold temperature stability or the tendency of retrogradation. For example, when the acetyl groups are introduced into the starch, reduction of gelatinizing temperature and improvement of cold temperature stability are

observed (Jarowenko, 1986). Sometimes, more than one modification are used on starch for a particular property (Wurzburg, 1986). For example, hydroxypropylation or acetylation and cross-linking are combined together to increase the freeze/thaw stability during frozen storage, because those modifications make the swollen starch granules intact and minimize or prevent loss in viscosity (Wurzburg, 1986). A combination of hydroxypropylation and cross-linking apparently provides the best freeze/thaw stability of surimi seafood (Park, 1995a). Pregelatinized starch is physically prepared by first heating the starch slurry above gelatinization temperature and then drying it. It can be rapidly rehydrated regardless of water temperature at room temperature for instant food (Whistler and Daniel, 1985). However, this pregelatinized starch negatively affects the gelation of surimi proteins. Fast rehydration of starch granules keeps proteins from being hydrated and functional.

Rheological properties of the gel

Rheology is defined as the study of material deformation and flow (Hamann and MacDonald, 1992). In surimi and surimi seafood, rheology is primarily used to investigate gel structure as it responds to applied forces and/or deformation. There are four reasons to learn rheological properties of food (Muller, 1973):

1. To allow insight into the structure of the material, because the physical manifestation is due to its chemical network.

2. To improve quality control in the food industry.

3. To design machinery for handling solid foods.

4. To correlate consumer acceptance with some definite rheological property.

Upon thermal processing, proteins are denatured and form a three-dimensional structure called a gel. A gel is a continuous network of macroscopic dimensions immersed in a liquid medium exhibiting no steady-state flow (Ziegler and Foegeding, 1991). In other words, the gel is a form of matter intermediate between a solid and a liquid (Oakenfull, 1987), exhibiting both viscous and elastic properties (Hamann and MacDonald, 1992). In the gel, the liquid restrains the network from collapsing into a compact mass and the network restrains the liquid from flowing away (Tanaka, 1981). Thus, the gel, having a three dimensional polymeric network, retains significant amounts of liquid (water), but yet shows mechanical rigidity.

There are two ideal behaviors of materials. A pure elastic solid, Hookean solid, will be instantaneously and finitely deformed when applied with a force. It will instantaneously return to its original shape upon removal of the force. A pure viscous liquid, Newtonian liquid, will flow when applied with the slightest force, at a rate of flow proportional to the magnitude of the force. It can not recover its original state when the force is removed. The rheological properties of food gels are not as simple as Hookean solid or Newtonian liquid, but are intermediate between both ideal states presenting viscoelastic properties.

Rheological tests for gels are categorized by a small-strain or nondestructive test, and a large-strain or destructive test (Hamann, 1988). Small-strain test deforms a sample slightly without breaking it. In this kind of test, the deformation of the sample is only a small percentage of that deformation required to break it. Large-strain test deforms the material to the point of permanent structural change. In protein gelation, the result of small-strain test often depends on the functionality of proteins and other ingredients, processing conditions (time and temperature), and test conditions (Hamann, 1987). The result of large-strain test can correlate with sensory texture of the food and help to determine the acceptability of foods (Montejano et al., 1985). Both tests can reveal the micro- and macro-structure of the gel. Rheological models, e.g. Maxwell model and Kelvin model, are commonly used to characterize the viscoelastic properties of foods and to predict their behavior under special physical conditions (Rao and Skinner, 1986). The model contains various combinations of Hookean solid elements (spring) and Newtonian fluid elements (dashpots). It can represent complicated viscoelastic behavior of different food materials.

Stress relaxation, which is one of transient tests for viscoelasticity (Steffe, 1992), is a small-strain test (Hamann and MacDonald, 1992). In stress relaxation test, the sample is suddenly brought to a given deformation (strain) and the same strain is maintained. The stress is measured as a function of time (Mohsenin, 1986). The stress will decay to an equilibrium value. An ideal elastic solid does not exhibit stress relaxation, while an ideal fluid with no internal structure relaxes instantaneously. Most food materials show

viscoelastic solid or elasticoviscous liquid behavior and constantly their stress relaxation pattern falls somewhere between that of ideal elastic solids and that of pure fluids (Peleg, 1979; Shama and Sherman, 1973). The relaxation behavior depends upon their internal structure. Thus, measuring the relaxation behavior can give the internal structure of the food. The result of stress relaxation can be expressed in terms of time-dependent modulus E(t) in tension or compression, G(t) in shear, or K(t) in bulk compression (Mohsenin, 1986). Furthermore, relaxation time, which represents the dissipation stress of the sample after receiving a sudden force, can be obtained.

Rheological parameters can be used to evaluate the texture of foods (Hamann, 1988). It is critical for all foods that the texture exhibits proper hardness (strength) and cohesiveness (deformability). The results of small-strain test may not correlate well with the texture, or hardness and cohesiveness in the sensory evaluation (Hamann, 1987). However, large-strain or fracture test can show those properties of the food and indicate the sensory quality of the food (Montejano et al., 1985). Torsion fracture test is widely used to measure the texture of surimi products (Hamann and MacDonald, 1992). Surimi gel is homogeneous and isotropic, so its mechanical characteristics of the texture is easily represented by fracture shear stress and fracture shear strain. Torsion testing of gels allows to measure fracture shear stress and fracture shear strain of the sample unambiguously because the sample is deformed without changes in specimen shape or volume, which can result in artifacts during compression and puncture testing (Hamann and Lanier, 1987). Fracture shear stress indicates hardness of the gel, and fracture shear

strain indicates cohesiveness, are obtained from torsion test (Montejano et al., 1985). Fracture shear stress is sensitive to protein concentration, processing conditions, and ingredients variables, while fracture shear strain is less sensitive to those factors and depends on protein quality affected by denaturation (Hamann, 1988).

Microstructure of the gel

An appreciation of the microstructure of food and its component is recognized as a necessary prerequisite for understanding its physical properties (Aguilera and Stanley, 1990). Development of new foods from refined protein sources requires a basic understanding of the interactions among components and their microstructural formation. Microscopy is a valuable analytical tool to investigate the network structure of the gel (Dziezak, 1988; Kaláb et al., 1995), and can help to understand the physical and rheological properties of food materials (Davis and Gordon, 1984; Kazemzadeh et al. 1982). A single technique can not fully characterize the properties of foods. Macrostructural evaluation of a gel usually involves the determination of some chemical or physical properties of the system, such as gel strength. On the contrary, microstructural evaluation involves monitoring reactions and observing physical changes of structures at a level that can not be directly observed by the human eye (Davis and Gordon, 1984) and facilitate the understanding of conformational, structural, chemical and physical properties of the food. Visual changes due to processing (gelatinization of starch,

gelation of protein, proteolysis of proteins) are the results of the change at the microscopic and molecular levels (Kaláb et al., 1995).

Traditionally, the structure of foods has been studied through the use of images enhanced by glass lenses, called optical microscopy. Because of advances in this area, the smallest observing size is 1,000-3,000 Å for ordinary or polarized (visible) light microscopy and fluorescence (ultraviolet) microscopy, about 150-200 Å for scanning electron microscopy, and about 2-5 Å for transmission electron microscopy (Davis and Gordon, 1984). The scanning electron microscopy can investigate three-dimensional structure of food. Using such technique, Yongsawatdigul et al. (1995) observed different microstructure of whiting surimi gel processed by conventional heating (slow rate) or ohmic heating (rapid rate). With assistance of the computer, image analysis can give quantitative information about microstructure of foods. When non-fish proteins or other ingredients are added into surimi seafood, the microstructure and rheological properties of the product are changed. Light microscopic graphs revealed thermal expansion of starch granule in the matrix of surimi gel, resulting in increased gel strength (Kim and Lee, 1987). Image analysis quantitatively indicated what difference between "set" and "no set" influences in the expansion of the starch granule, resulting in different texture of surimi-starch gels (Kim and Lee, 1987).

Chapter 3

Effects of Starch Properties and Thermal Processing Conditions on Surimi-Starch Gels

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Abstract

Effects of starch and thermal conditions on texture, microstructure, and color of surimi-starch gels were investigated by measuring shear stress, shear strain, color values as well as microstructure. The effect of starch on texture of surimi-starch gels depended on the concentration and modification of starch as well as the ratio of amylose and amylopectin. The lower starch concentration increased surimi-starch gels strength more effectively. Modification facilitated starch granules to swell easily and increased shear stress. The more amylopectin in starch, the stronger surimi-starch gel. Conversely the more amylose, the weaker the gel. The influence of heating temperature on texture depended on the gelatinization temperature of the individual starch. A longer heating time slightly increased shear stress of surimi-starch gels. Shear strain values of surimi-starch gels were not affected by heating time and temperature, but depended on gelatinizing properties of starch. The larger granules of starch, observed by light microscope, resulted in stronger gels. Higher heating temperature caused granules to become bigger for native starches, but did not affect modified starches. The color (L* and b*) of surimi-starch gels also depended on concentration and properties of starch. The more the granule swelled, the lower the L* value and the b* value of gels.

Key Words: texture, color, surimi, starch, microstructure.

Introduction

Surimi (mechanically deboned, washed, and cryostabilized fish proteins) is used as a primary functional ingredient for crabmeat analogs (hereafter surimi seafood). Starch, a natural macropolymer of glucose synthesized by plants, is the second most important ingredient in surimi seafood. Starch, insoluble in cold water, can be easily dispersed during chopping, and then renders functionality by heating. Thermal processing causes the granules to swell, absorb water, and impart viscosity (Sanderson, 1990). Starch is valued as a functional food additive because of its contribution to texture. When starch is added into surimi seafood, it modifies texture, improves freeze-thaw stability, and decreases the cost (with addition of water) (Lee et al., 1992; Wu et al., 1985a). In a composite food like surimi seafood, the texture can be controlled not only by protein additives, but also by starches. Park (1995b) reported that gel strength greatly increased when surimi was replaced by the same amount of starch. The starch granule is chemically (amylose and amylopectin) and physically (amorphous and crystalline phase) heterogeneous (Wang et al., 1989). In the cold water-starch system, the starch granules can reversibly absorb water, swell slightly and become partially hydrated upon excessive comminution (Waniska and Gomez, 1992; Whistler and Daniel, 1985). As they are heated, irreversible swelling of starch granules occurs. If the heating continues to reach gelatinization temperature (GT), the granules absorb more water and the viscosity dramatically increases (Morris, 1990; Waniska and Gomez, 1992). In the surimi-starch system, thermal changes of the starch granule are different from the starch-water system.

During thermal gelation of fish proteins, gelatinization of starch occurs concomitantly. However, it is delayed by myofibrillar proteins, salt, sucrose, and sorbitol in the surimi-starch system. Myofibrillar proteins are thermally denatured before the starch is completely gelatinized (Wu et al., 1985a). Water is entrapped in the protein gel network limiting the availability of water for starch gelatinization, resulting in competition for water between starch and proteins (Kim and Lee, 1987). Starch granules swell in water and expand themselves until they are limited by the gel matrix. In surimi seafood, the granules can not expand as large as in the starch-water system (Okada and Migita, 1956), resulting in a reinforcing or pressuring effect on the gel matrix and the higher gel strength (Lee et al., 1992). However, the gel strength can decrease if too much starch is added (>80 g/kg) (Lee and Kim, 1986b; Park et al., 1997). Different botanic sources of starches behave differently in the texture of surimi-starch gels. Potato starch increases the gel strength more than corn starch, possibly due to the size of the granule (Lee, 1984). Therefore, gelatinization of starch plays an important role in the formation of a network structure of surimi-starch gels. The ratio of amylose and amylopectin varies among different starches. Amylose and amylopectin behave differently during gelatinization (Morris, 1990). Modification makes the functional properties of starch different from its native starch. Gelatinization of starch in the protein gel is influenced by heating temperature, degree of swelling, and water uptake of the starch granule (Wu et al., 1985b). Temperature and time are two of the most important factors that influence gelatinizing properties of starch and gelation properties of fish proteins in the surimi-starch system. Thus they determine the texture of surimi-starch gels. However, most

studies on surimi-starch gels have concentrated on the effect of an individual starch at a fixed heating temperature and time. It has not been clearly stated how the interaction of heating temperature and time affect the physical properties of surimi-starch gels. The objective of this study was to determine effects of starch properties and thermal processing conditions such as heating time and temperature on texture, microstructure, and color of surimi-starch gels.

Materials and Methods

Materials

High grade Alaska pollock (*Theragra chalcogramma*) surimi kept frozen for about six months was obtained from Trident Seafood Corporation (Seattle, WA). Surimi was cut into about 1,000 g blocks, vacuum-packaged, and stored in a freezer (-25°C) throughout the experiments. Five starch samples were used for the experiment. Native potato starch (PS) and potato starch modified with acetylation (MPS) were obtained from Roquette America, Inc. (Keokuk, IA). Native corn starch (CS) and two modified waxy maize starches (MWMS-I and II) were obtained from Cerestar (formerly American Maize-Products Company, Hammond, IN). MWMS-I containing amylopectin (1000 g/kg) was cross-linked by adipic acid anhydride and tested as a high amylopectin starch. MWMS-II containing amylose (450 g/kg) and amylopectin (550 g/kg) was hydroxypropylated and was tested as a high amylose starch.

Gel preparation

Sample preparation was made based on test formulation (Table 3.1). Frozen surimi was tempered at room temperature for 2 hr before cutting into about 3 cm cubes. Surimi cubes were placed in a Stephan vacuum cutter UM-5 (Stephan Machinery Corp., Columbus, OH). In the first 1.5 min, frozen cubes were chopped at low speed. Salt (20 g/kg) was sprinkled in and chopping continued at low speed for 0.5 min. Ice/water with or without starch (0, 30, 60, and 90 g/kg) was added to adjust the moisture level to 780 g/kg to maintain gels at an equal moisture content and chopped at low speed for 1 min. For the final 3 min, chopping continued at high speed while vacuum maintained at 0.5-0.6 bar. During chopping, a constant cold temperature (<8°C) was maintained using a NesLab chiller (NesLab, Portsmouth, NH). The paste was stuffed into stainless steel tubes (inner diameter = 1.9 cm, length = 17.5 cm) with stainless steel screwable caps, using a sausage stuffer (Sausage Maker, Buffalo, NY). The interior wall of the tubes was coated with a film of PAM cooking spray (Boyle-Midway, Inc., New York, NY). The tubes were heated in a water bath at either 70° or 90°C for either 20 or 60 min. Cooked gels were chilled quickly in ice water. The gels were kept refrigerated overnight.

Torsion tests

Cold gels (5°C) were placed at room temperature for 2 hr. The gels were cut into a piece (length = 2.9 cm) and milled into a dumbbell geometry (end diameter = 1.9 cm and minimum diameter at center = 1.0 cm). Shear stress and shear strain of the sample at mechanical failure were measured using a torsion gelometer (Gel Consultants,

Inc., Raleigh, NC) set at 2.5 rpm (NFI, 1991). Failure shear stress was measured to determine the strength of gels, while failure shear strain was measured for the deformability of gels. Ten samples were measured and the average values were reported.

Table 3.1. Experimental formula (g/kg).

Ingredients	A	B	C	D
Surimi	800	680	560	440
Water/ice	180	270	360	450
Salt	20	20	20	20
Test starch	0	30	60	90
Total	1000	1000	1000	1000

Each formula was based on equal moisture (780 g/kg) and salt (20 g/kg).

Color measurement

Gels were equilibrated to reach room temperature and the color was measured according to a method described by Park (1995c). Color L* (lightness) and b* (yellowness "+" or blueness "-") were measured by a Chroma Meter (Model CR-310, Minolta Corp., Ramsey, NJ) to evaluate the effects of heating time and temperature as well as type and concentration of starch. Color a* was not reported because it is very consistent for surimi gels regardless of processing parameters and moisture content (Park, 1995c). Five gel samples were used for color analysis.

Microstructure

A light microscope was used to observe physical structure of starch granules (30 and 90 g/kg) in surimi gel cooked at 70° and 90°C for 20 min. Small gel blocks (0.5 cm^3) were frozen in a freezer (-70°C) over night and rapidly sectioned with a surgical knife. Prepared sections were mounted on Gold Seal micro slides (Dickinson and Company, Franklin Lakes, NJ). They were dehydrated first by dipping the specimen in 500 ml/L ethanol and then in 700 ml/L ethanol. The protein was stained 1 g/L Eosin Y in ethanol (700 mL/L) for 10 min, and the excess stain was rinsed off first with 700 mL/L, then with 500 mL/L ethanol and finally with water. Starch granules were stained by iodine vapor as described by Little (1957). When thoroughly dried, the slides were mounted in VAN-LAB micro cover glasses (VWR Scientific, San Francisco, CA). The prepared specimens were observed using an Olympus microscope at 200X (Model BHT, Tokyo, Japan) and the images were photographed using an Olympus OM-1 camera (Tokyo, Japan).

Statistical analysis

All experimental runs were repeated three times. The main effects and second-order interaction effects based on a split-plot design were analyzed using ANOVA (Petersen, 1990). Starch concentration, heating temperature, and replication were plots. Heating time was subplot. The error term for the plot was Repeat*Concentration* Temperature. The error term for subplot was Repeat*Concentration*Temperature*Time.

All statistical analysis were achieved using SAS PROC ANOVA (SAS Institute Inc., Cary, NC).

Results and Discussion

As a function of textural properties, shear stress represents gel strength. Shear stress values were significantly affected by starch concentration ($P<0.0001$), except MWMS-I ($P>0.05$) (Table 3.2). When surimi paste with 30 g/kg starch concentration were heated at 90°C, the highest value of gel strength was obtained, except PS (Fig. 3.1). With PS, the highest value of shear stress was obtained at 60 g/kg concentration. When more starch was added, the values of shear stress decreased, except MWMS-I. The values

Table 3.2. Statistical difference of shear stress as affected by heating temperature, heating time and starch concentrations.

	Temperature	Time	Starch content
PS	+++[4]	++[3]	+++
MPS	-[1]	++	+++
CS	+++	+[2]	+++
MWMS-I	-	++	-
MWMS-II	-	+	+++

1. '-' means $P>0.05$
2. '+' means $0.01<P<0.05$.
3. '++' means $0.001<P<0.01$.
4. '+++' means $P<0.001$.

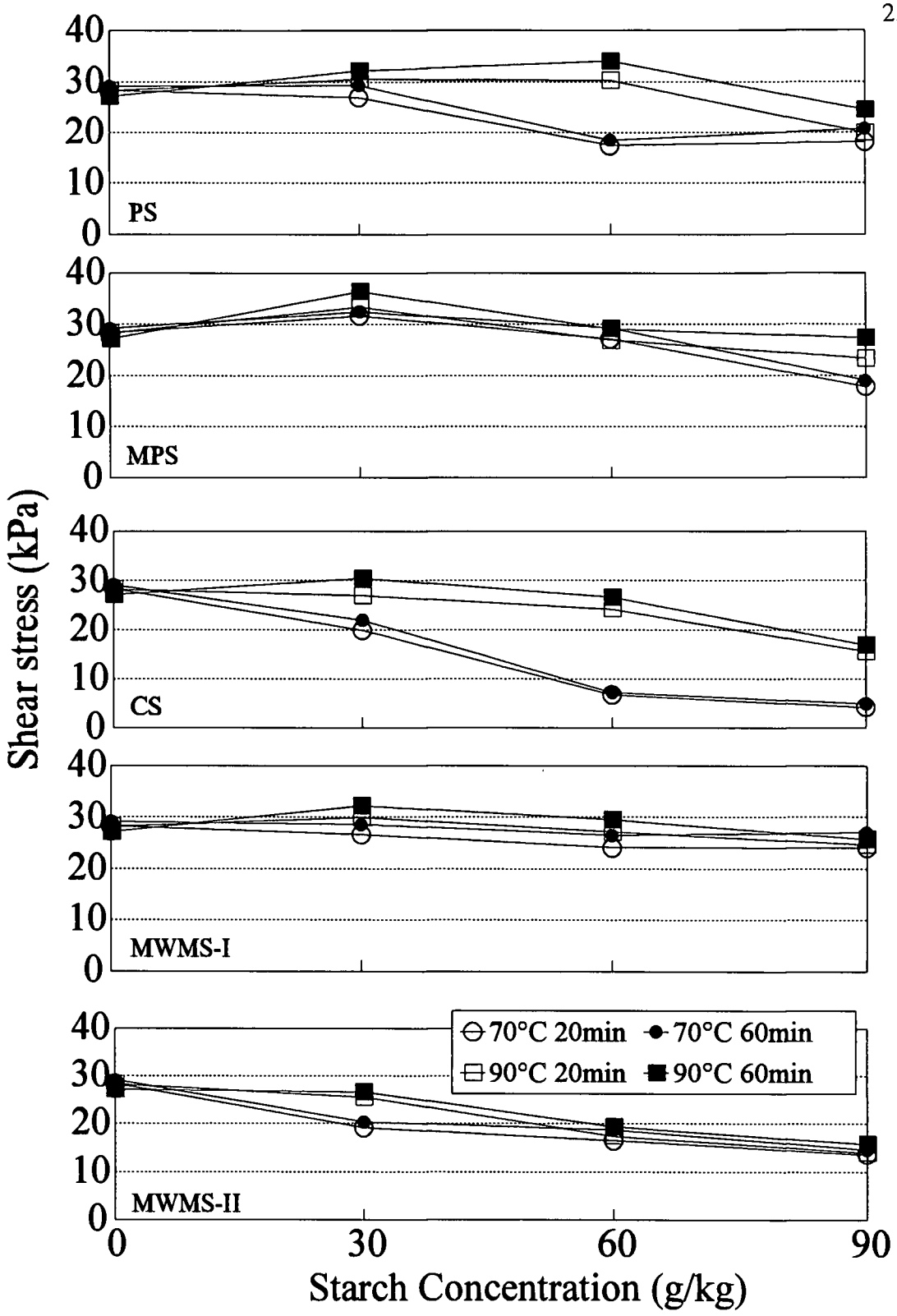

Figure 3.1. Shear stress of the surimi-starch gels affected by heating time, and temperature, and starch concentration.

of shear stress of the gel with MWMS-I did not change ($P>0.05$), even at higher starch concentration (90 g/kg). The results were very similar to those of Park et al. (1997). Upon the addition of low starch concentration, shear stress increased. Shear stress decreased gradually when the starch concentration continuously increased. The textural characteristics of protein gels containing fillers depend on the molecular structure of the filler which can either depress or reinforce the primary gel structure (Aguilera and Kessler, 1989). As starch granules absorb water from the surrounding during heating, the expanded starch granules give pressure to the gel matrix, resulting in increased gel strength (Lee et al., 1992). At higher starch concentration (90 g/kg), the concentration of the myofibrillar proteins, mainly forming gel structure, was greatly diluted (from 800 to 440 g surimi /kg) (Table 3.1). It resulted in weaker gel network, representing the properties of the "starch" gel (Park et al., 1997). The swollen granules interfered with the formation of a fish protein network. Thus the values of shear stress were lower at the high starch concentration (90 g/kg). When starch concentration was raised from 30 to 90 g/kg, available moisture to the starch decreased (30 g starch/780 g water to 90 g starch /780 g water). In the starch-water system, such a decrease in moisture does not change the physical properties, such as glass transition temperature (T_g) (Biliaderis, 1992). However, in the surimi-starch system, there were not only starch and water, but also fish proteins, salt, and sugar components. Proteins can bind water during thermal denaturation, which occurs prior to starch gelatinization (Wu et al., 1985a). Those proteins could bind a majority of water leaving less water available for starch than in the starch-water system. Sucrose acts as an anti-plasticizer and increases T_g of starch

granules, resulting in elevated gelatinization temperatures (Eliasson, 1992). Thus it was possible that T_g increased in the surimi-starch system resulting in the delay of melting crystallites or swelling of starch granules. The gel strength decreased when such effect was more than the reinforcing effect. Therefore, the low starch concentration (30 g/kg) had relatively more water available and the granules probably had lower GT than the high starch concentration (90 g/kg). The high starch concentration had relatively less water available and the granules probably could have higher GT. The swelling ability decreased and formed the weak gel. Shear stress values were affected by heating time ($P<0.05$) (Fig. 3.1, Table 3.2). The gel strength slightly increased as heating time was prolonged from 20 to 60 min. Longer heating time might possibly make starch granules absorb more water and enlarge themselves for a firmer texture.

Heating time (20 and 60 min) and temperature (70° and 90°C) did not affect shear stress values of pure surimi gels. It elucidated that fish proteins complete the gel formation at 70°C within 20 min. Two native starches (PS and CS) had a different effect on shear stress of the gels between 70° and 90°C ($P<0.05$) (Fig. 3.1). When heating temperature increased, the swelling power also increased (Lii et al., 1995). The higher temperature resulted in more pressure into the gel matrix. However, shear stress values of surimi gels containing modified starches (MPS, MWMS-I, and MWMS-II) were not much affected by the two different heating temperatures ($P>0.05$) (Table 3.2). It could be due to the modification, which changed the structure of starch granule from its native stage and decreased GT. At 70°C, shear stress of gels with CS continued to decrease as

starch concentration increased, resulting in extremely soft gels (<5 kPa) at 90 g/kg concentration. At 30 g/kg starch addition, neither PS, MPS, nor MWMS-I changed the shear stress values of gels cooked at 70°C. The internal structure of the granule probably influenced the texture of surimi-starch gels, especially at the low heating temperature (70°C). Normally, cereal starches except waxy starches have lower swelling ability than root and tuber starches (Jarowenko, 1986). Between the two native starches, PS has weaker internal molecular structure within the granule than CS, so PS requires lower GT and swells much more rapidly and redundantly than CS (Jarowenko, 1986; Kokini et al., 1992). Swelling power is more than 1,000 for PS, and is just 24 for CS (Jarowenko, 1986). In the starch-water system, GT is about 56°-66°C for PS and 62-72°C for CS (Leach, 1965). However, the starch gelatinization is delayed in surimi seafood, due to the presence of myofibrillar proteins as well as other food additives (salt, sucrose, sorbitol, etc). Although GT of PS was elevated to higher temperature in surimi-PS system, PS granules probably swelled redundantly even at low temperature (70°C), so the gels still showed high shear stress values. However, the swelling ability of CS might have greatly decreased in surimi-CS system, so the gels showed much lower shear stress values. The gels with MPS at 30 g/kg had higher shear stress than those with PS (Fig. 3.1). The acetylation decreases GT of starch and increases swelling ability (Jarowenko, 1986). Thus, MPS with low GT could swell at lower temperatures and absorb more water than PS. On the other hand, the mechanical strength of starch granules is positively related to its reinforcing effect on surimi gels (Okada, 1963). Acetylation can increase the stability of starch granules against external shear force (Jarowenko, 1986). Therefore,

MPS could greatly increase the reinforcing effect on the gel matrix even at a lower temperature (70°C). Because of lower GT for MPS granule, 70° and 90°C did not cause any differences ($P>0.05$) in shear stress values of gels (Table 3.2). It demonstrated that the effect of heating temperature on surimi-starch gels depended on the properties of the starch, and the internal molecular structure of the granule and GT.

Unlike MWMS-I, MWMS-II did not appear to positively interact with surimi proteins. Shear stress values continued to decrease as the level of starch concentration increased (Fig. 3.1). It was possibly caused by the high amylose concentration (450 g/kg) which influenced the formation of the gel structure. During the gelatinization, amylose leaches out from the starch granules and forms the starch gel matrix while amylopectin remains within the swollen granule in the starch-water system (Morris, 1990). The effect of the starch on surimi-starch gels might be affected by amylose and amylopectin components in starch granule. Swelling is an attribute of the amylopectin and the effect of amylose on the swelling of granules is a diluent (Tester and Morrison, 1990). The higher the proportion of branching (more amylopectin), the less firm the structure of the granule (Biliaderis et al., 1980) and the higher swelling power (Leach, 1965). The swelling ability is much lower and GT is much higher for high amylose starch (Whistler and Daniel, 1985; Jarowenko, 1986). When the temperature is raised above GT, hydrogen bonds in the starch granule continue to be disrupted, water molecules become attached to the liberated hydroxyl groups, and the granules continue to swell (Whistler and Daniel, 1985). If the concentration of amylose was increased, more amylose could probably be

leached from the granule when heating temperature was above GT. Even though those leaching amylose groups were attached to some water by hydrogen bonds, this type of water could not contribute to the enlargement of the granule because it was inter-granule. Amylose stabilizes the starch granule during thermal swelling (Biliaderis et al., 1980). Amylose probably reduced the amylopectin's swelling ability of the granule and limited expansion of the granule. Therefore, from shear stress values of gels with MWMS-II, it was demonstrated that amylose greatly depressed the effect of the starch granule's reinforcement on the gel structure and resulted in reduced gel structure. However, MWMS-I (Fig. 3.1) had the ability to reinforce the gel structure possibly because of its 1000 g/kg amylopectin component as well as modification (cross-linking) which greatly increased the mechanical strength or the stability of starch granules (Whistler and Daniel, 1985; Wurzburg, 1986). The higher the concentration of amylopectin, the more water was absorbed and the bigger the granule was obtained. The gel strength was consistently maintained when MWMS-I was added to replace surimi. The effect of amylopectin on the surimi-starch gel strength was opposite to amylose. The hydroxypropylation decreases GT of starch granule and increase swelling ability (Tuschhoff, 1986). It caused MWMS-II to start swelling at lower temperatures, so there was no difference between both heating temperatures ($P>0.05$). Such modification resulted in more water absorbed by MWMS-II granule than the native CS at 70°C. Thus shear stress values of the gel with MWMS-II (60 and 90 g/kg) were much higher than CS at 70°C. When heating temperature was increased to 90°C, the granule of CS could absorb more water than at 70°C. However, the granule of MWMS-II could not take more water from the surroundings due to the

depression by high amylose content at 90°C, compared to 70°C. Shear stress of the gel cooked at 90°C with CS was much higher than the gel with MWMS-II. Therefore, the effect of amylose component in the starch on surimi-starch gels might be more than that of modification.

Table 3.3. Statistical difference of shear strain as affected by heating temperature, heating time and starch concentrations.

	Temperature	Time	Starch content
PS	-[1]	-	-
MPS	-	-	-
CS	-	-	+[2]
MWMS-I	-	-	-
MWMS-II	-	-	-

1. '-' means $P>0.05$
2. '+' means $0.01<P<0.05$.

There was no significant difference between shear strain values as affected by different heating times, temperatures, and starch concentrations, with the exception of CS (Fig. 3.2, Table 3.3). The shear strain values were significantly affected by the starch concentrations when CS was added into surimi ($P<0.05$). With CS (Fig. 3.2), shear strain of the gel decreased when surimi mixed with high concentration of starch (60 and 90 g/kg) was heated at 70°C, resulting in a less cohesive gel structure. Since CS apparently has the highest GT among test starches, the formation of gel structure was limited because the CS granule could not swell at low heating temperature. For other starches, shear

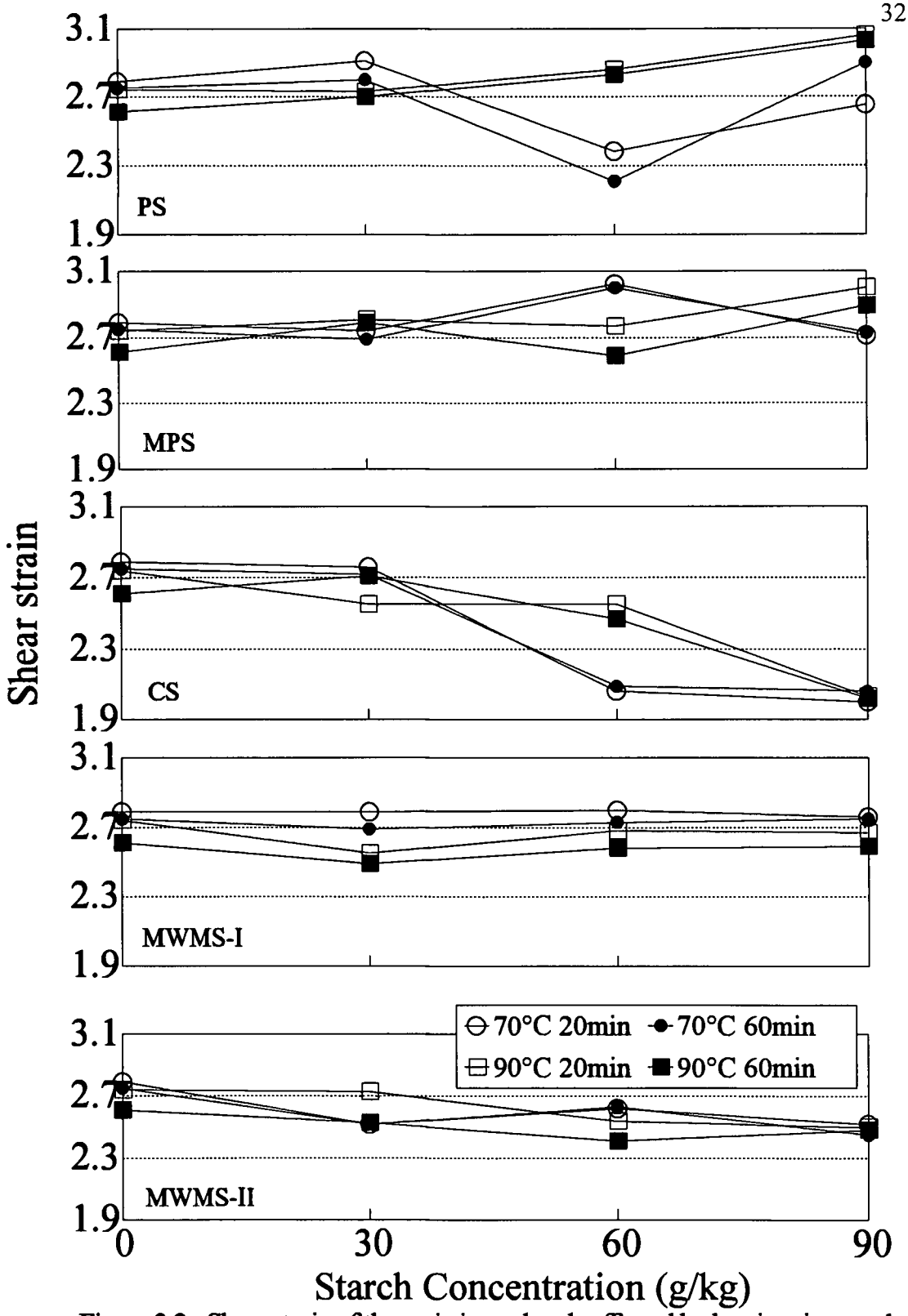

Figure 3.2. Shear strain of the surimi-starch gels affected by heating time, and temperature, and starch concentration.

strain did not change. Their granules had low GT because of modification (MWMS-I, MWMS-II, MPS), weak internal structure (PS), or more amylopectin content (MWMS-I). Thus those granules could be gelatinized at low heating temperature and maintained the higher value of shear strain, like gels with surimi only. Shear strain of surimi gel is not sensitive to protein concentration, processing conditions and ingredient variables but is rather a function of protein quality (Hamann, 1988). In the surimi-starch gels, the properties of starch including GT appeared to affect shear strain values. If the starch granule did not swell enough, shear strain of gels could be low. Even if there were no statistical differences ($P>0.05$), shear strain values gradually increased with PS and MPS; decreased with CS and MWMS-II; and remained constant with MWMS-I, as the starch concentration increased (Fig. 3.2).

The integrity of starch granules was maintained at 70° and 90°C, but the size was different among starches (Fig. 3.3 A-E). The size of granules is one of the most important properties in reinforcing the gel matrix (Aguilera, 1992). MPS had the largest granule (Fig. 3.3-B) because the internal structure had changed through modification with acetylation. The microscopic size of starch granules was not affected by heating temperatures for modified starches (MPS, MWMS-I and MWMS-II) (Fig. 3.3-B, D, E). However, with PS (Fig. 3.3-A) and CS (Fig. 3.3-C), the size of the granules was quite different at two heating temperatures, especially CS. It illustrated that the granule's swelling might be dependent on the molecular structure within the granule. Since the internal structure was changed by modification, the granule could more easily swell and

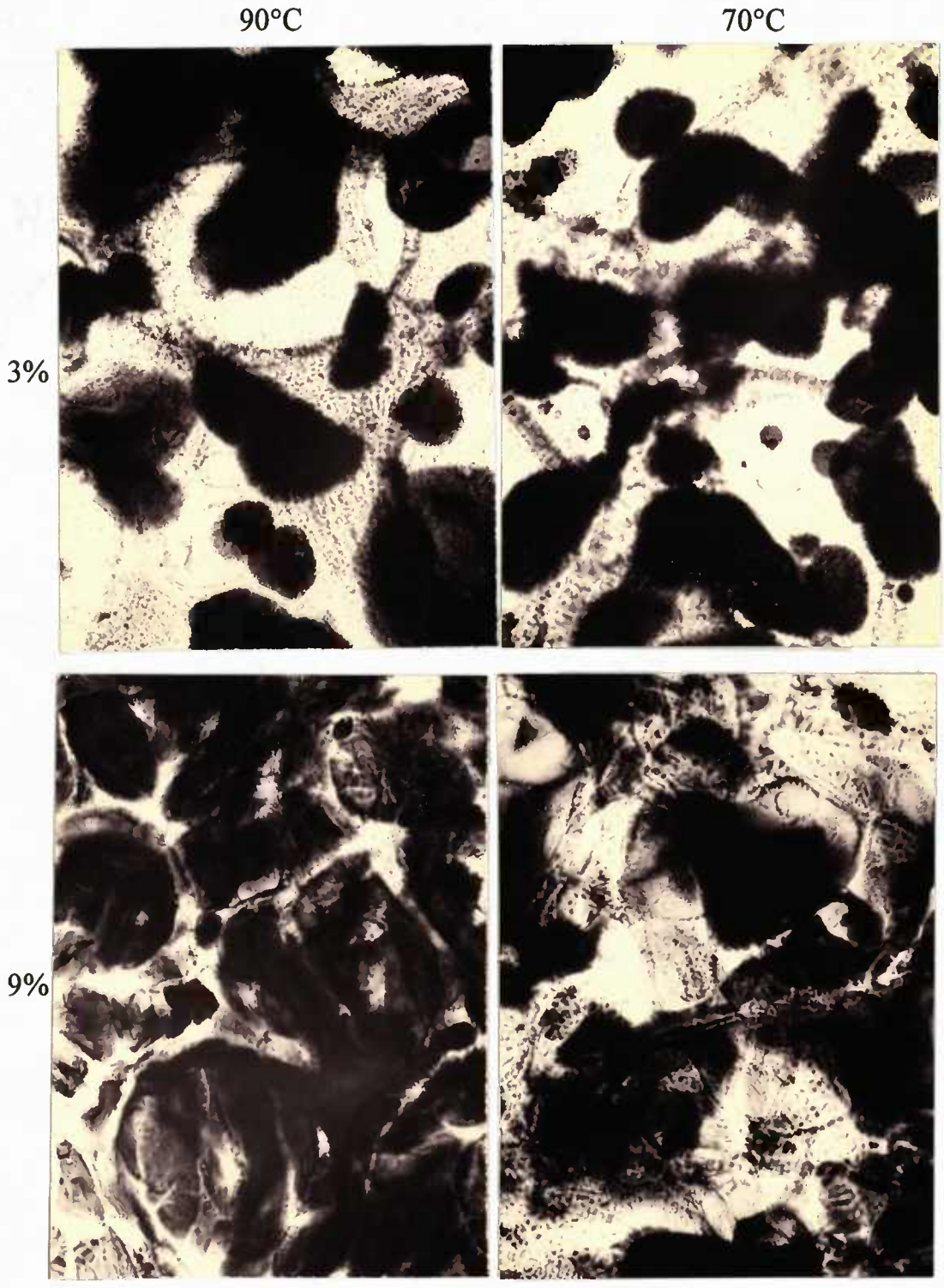

Figure 3.3-A Microstructure of PS granules in the gels.

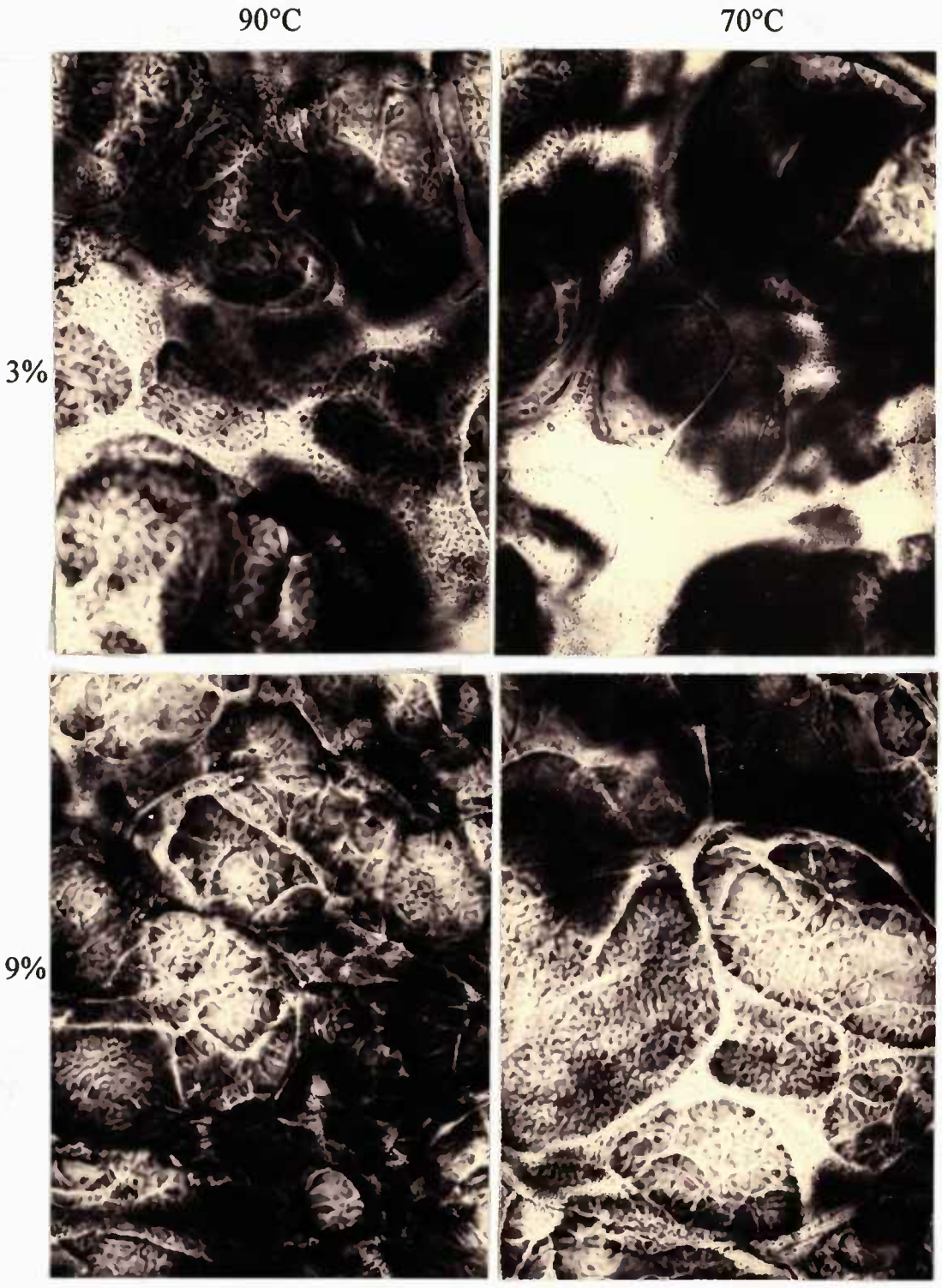

Figure 3.3-B Microstructure of MPS granules in the gels.

200μm

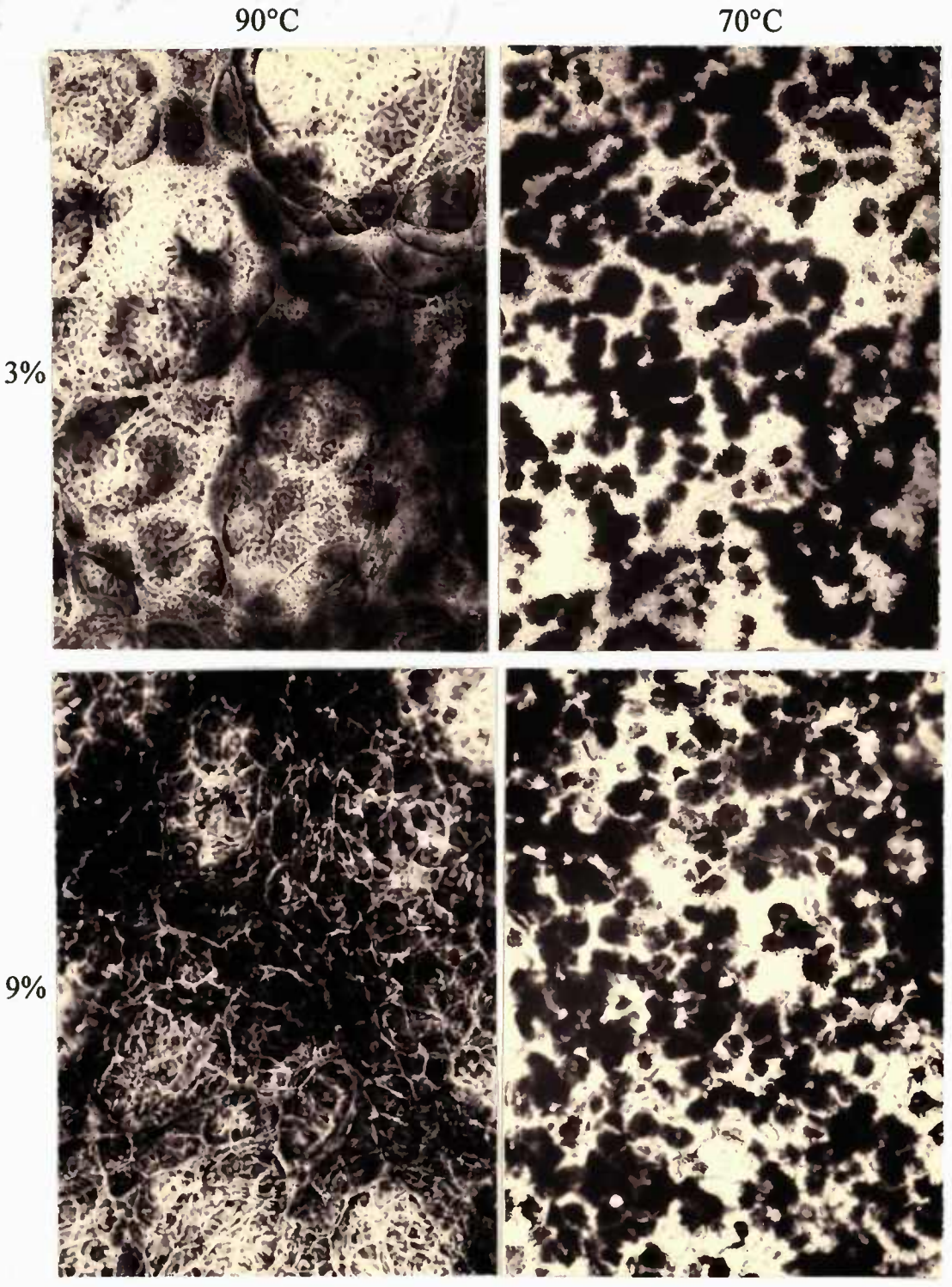

Figure 3.3-C Microstructure of CS granules in the gels. 200μm

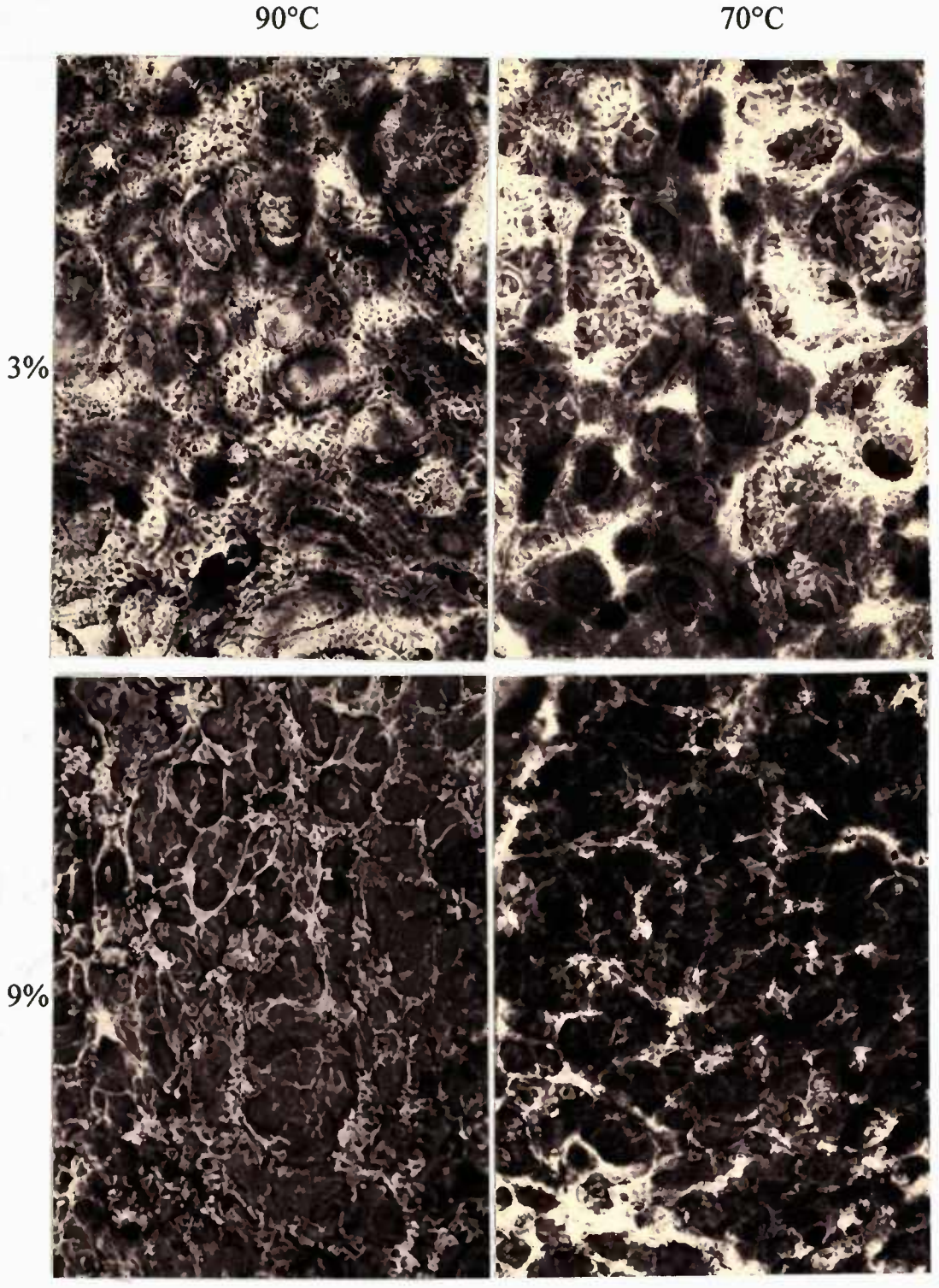

Figure 3.3-D Microstructure of MWMS-I granules in the gels.

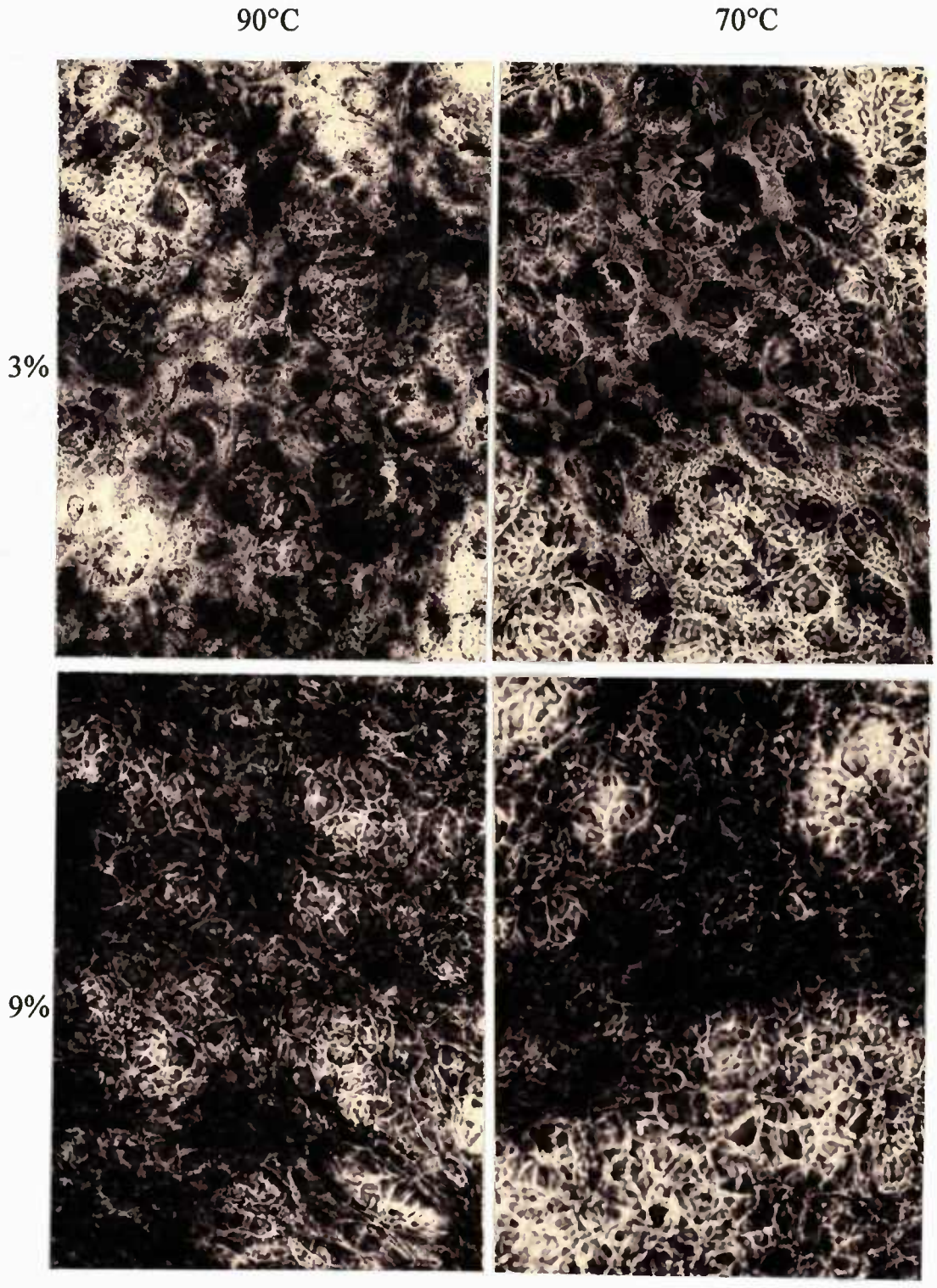

Figure 3.3-E Microstructure of MWMS-II granules in the gels.

expand itself even at 70°C than its native starch, (i.e., PS vs. MPS). The microstructure showed that the size of the granules were larger at low starch concentration (30 g/kg) than at high starch concentration (90 g/kg), especially with the native starch. The size of CS granule was smallest at 90 g/kg concentration and 70°C. It supported the weak structure of the gel with lower shear stress (Fig. 3.1) and lower shear strain (Fig. 3.2). Compared with the values of shear stress (Fig. 3.1), the larger the size of granule, the higher the value of shear stress. Factors affecting gel strength seemed to be more than the size of starch granule itself. Although the granule size of MWMS-I was not as large as MPS, the ability to increase the gel strength was almost the same (Fig. 3.1). It demonstrated amylopectin component of the granule could be an additional factor to increase the gel strength. Starch granule is "filled" in the gel matrix (Lee et al., 1992). According to the model of the filler gels (Aguilera and Kessler, 1989), the property of filler is classified into active and inactive. Starch granules in fish protein gels had active and inactive fillers. When the granules could not absorb enough water to produce reinforcement into the gel matrix, those granules inactively filled into the network and could not give pressure in the matrix, resulting in the weak gel, such as CS at 70°C. Once the granules were swollen, they were actively filled in the network and built pressure in the structure, such as CS at 90°C. Consequently, strong gels were formed. The use of microscope to examine the distribution of starch granules determined the status of starch in surimi gels, active or inactive (Fig. 3.4).

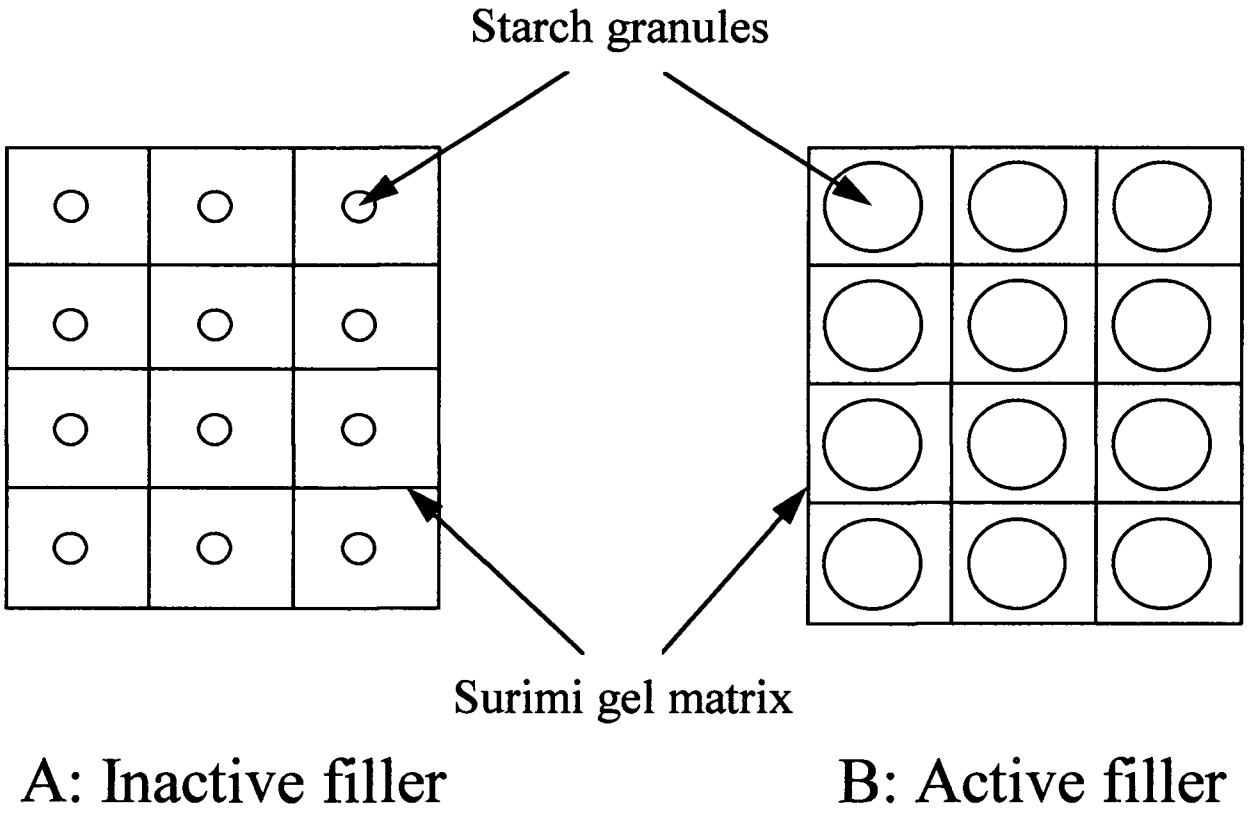

Figure 3.4. Swollen (active filler) and unswollen (inactive fillers) starch granules in surimi gel.

Table 3.4. Statistical difference of L* as affected by heating temperature, heating time and starch concentrations.

	Temperature	Time	Starch content
PS	-[1]	-	+++[4]
MPS	-	-	+++
CS	+++	-	+[2]
MWMS-I	+++	-	+++
MWMS-II	-	-	+++

1. '-' means P>0.05
2. '+' means 0.01<P<0.05.
3. '++' means 0.001<P<0.01.
4. '+++' means P<0.001.

The addition of starch into surimi influenced the color values of surimi gels (P<0.05) (Fig. 3.5, Table 3.4). Gel color is one of the quality parameters for surimi seafoods, as important as texture and flavor (Park, 1995c). When starch was added into surimi, L* value (lightness) of the gel decreased. As more starch was added in the gels, the gels exhibited low L* value or became more translucent, except CS at 70°C. Lightness of the gels with CS heated at 70°C increased when the concentration of starch increased. As mentioned above, CS granule was not gelatinized at 70°C (Fig. 3.3-C), and those unswollen granules inactively filled in the gel matrix. When CS concentration increased, more water was added into surimi (Table 3.1). However, most of water stayed merely out of starch granules. As a result, more light reflected from the inter-granule area or the gel matrix (Fig. 3.4). Thus lightness of surimi-CS gels increased or the gels exhibited more opaque when the unswollen starch concentration increased. The higher

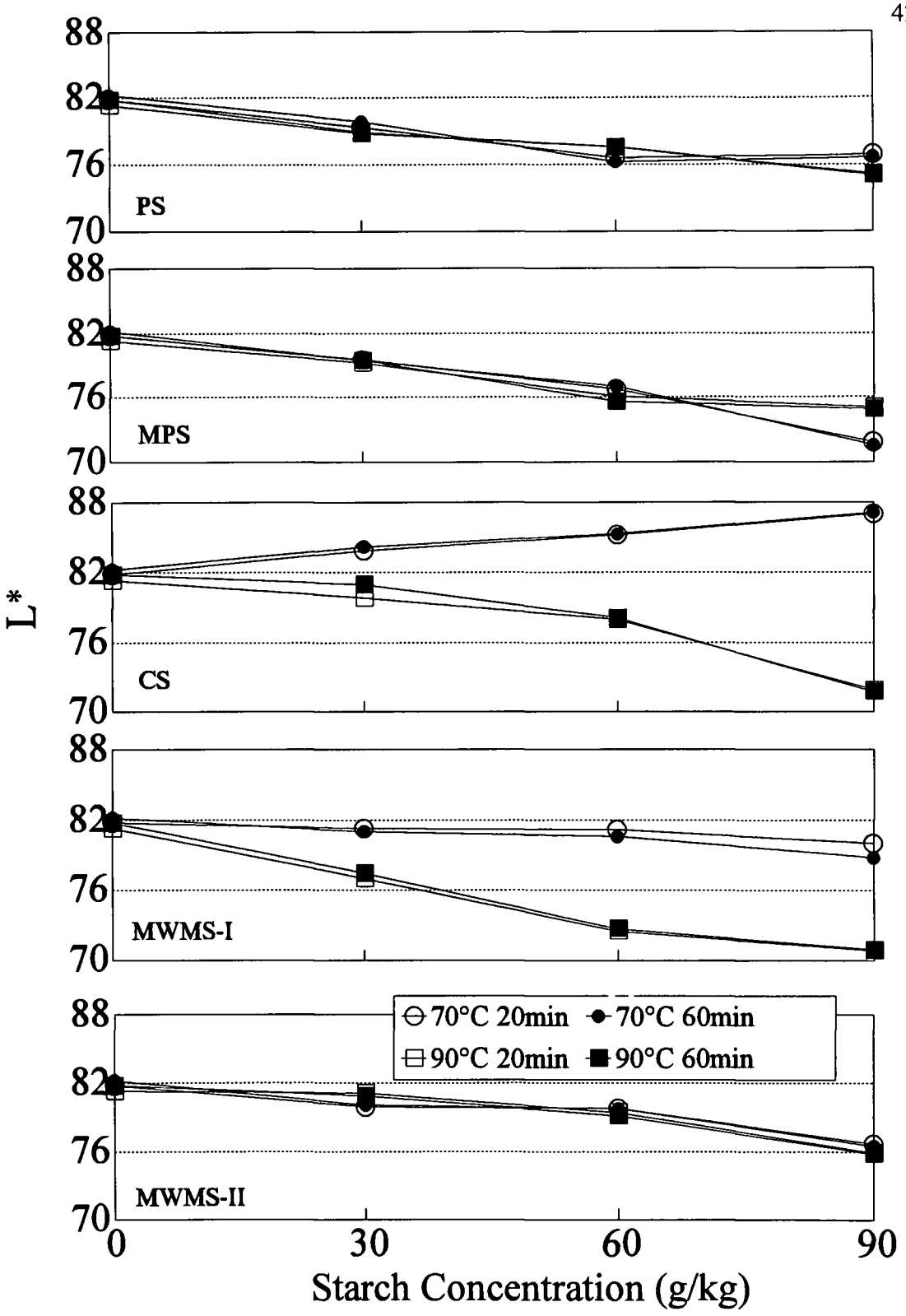

Figure 3.5. L* values of the surimi-starch gels affected by heating time, and temperature, and starch concentration.

the water concentration, the lighter (higher L* value) or the more opaque surimi gel (Park, 1995c). However, the color of the gels with starches (swollen) exhibited low L* values as the starch concentration increased (Fig 3.5). When their granules absorbed water and became fully swollen (Fig 3.4), more light could pass through swollen granules, demonstrating translucent gels (Charley, 1982; Leach, 1965). Therefore, L* value decreased when the starch concentration increased. At 90°C, L* value was highest with MWMS-II followed by CS and MWMS-I (Fig. 3.5). It was probably due to different swelling abilities of these granules and the amylose concentration of starch. The high concentration of amylose makes starch paste more opaque (Langan, 1986). It also made surimi-starch gels become more opaque or higher L* value when starch had high amylose concentration. At 70°C, the highest L* value was obtained with CS followed by MWMS-I and MWMS-II. CS probably had much lower swelling ability than MWMS-I and MWMS-II. L* value of PS was higher than MPS at both heating temperatures, especially at 90 g/kg. Acetylation increases the swelling ability of starch granules (Jarowenko, 1986) so that MPS granule could absorb more water than PS resulting in a more translucent color for surimi-MPS gels. Heating temperatures affected the color of gels with CS and MWMS-I ($P<0.001$). It also resulted from a different swelling ability of CS at both heating temperatures. Gels with MWMS-II, MPS and PS did not show any difference between 70° and 90°C ($P>0.05$). This trend might be due to the similar swelling ability at both heating temperatures. However, there was no significant effect ($P>0.05$) at different heating times on gel lightness for all surimi-starch gels. Generally, the more water was imbibed by the starch granules, the more translucent or the lower L*

values were obtained. Lightness of surimi-starch gels depended not only on starch concentration, but also the properties of starch: gelatinization and/or swelling ability.

Table 3.5. Statistical difference of b* as affected by heating temperature, heating time and starch concentrations.

	Temperature	Time	Starch content
PS	-[1]	-	-
MPS	-	+[2]	++[3]
CS	++	-	+
MWMS-I	-	-	+
MWMS-II	-	-	-

1. '-' means $P>0.05$
2. '+' means $0.01<P<0.05$.
3. '++' means $0.001<P<0.01$.

A significant difference in b* values (yellowness "+" or blueness "-") was observed with different starch concentrations, except PS and MWMS-II ($P<0.05$) (Fig 3.6, Table 3.5). When starch was added into surimi, b* value of the gel generally decreased, or the color slightly changed from yellow hue (+) to blue hue (-), except CS. The color value of b* with CS generally increased at 70°C, as the concentration of CS increased. It was strikingly different from b* values of surimi-CS gels cooked at 90°C. The properties of the granule swelling also affected b* values, as did the lightness of surimi-CS gels. Unlike other starches which changed b* values of gels from yellow to blue when the concentration increased, unswollen CS granules increased b* values. There was no significant difference between both heating temperatures, except CS ($P<0.01$). CS

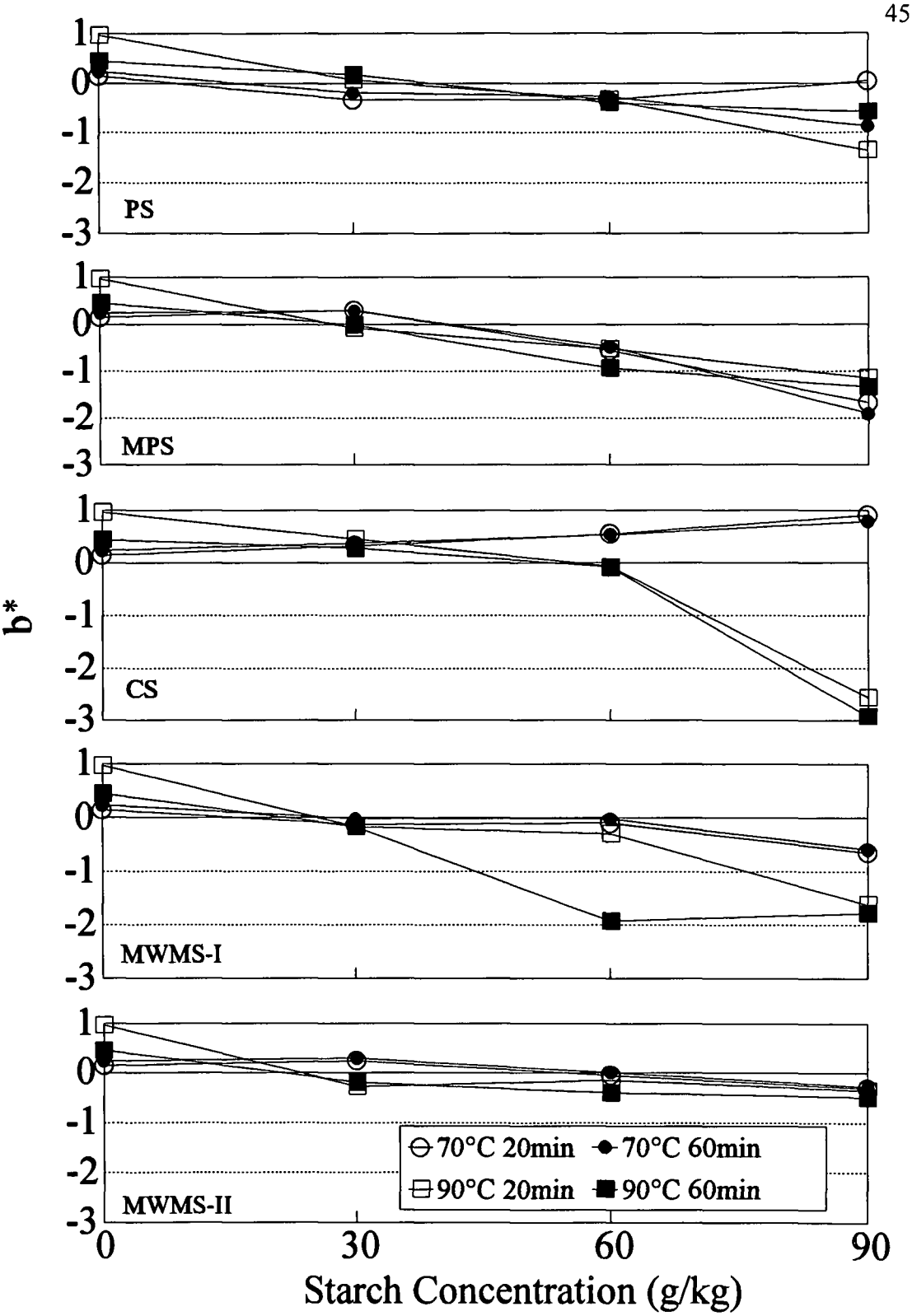

Figure 3.6. b* values of the surimi-starch gels affected by heating time, and temperature, and starch concentration.

granules had a different gelatinization property between 70° and 90°C (Fig 3.3-C), resulting in different b* values. The influence of starch on b* values of gels was not as obvious as that on L* values. There was no significant difference between different heating times, except MPS. Yellowness (b*) of surimi-starch gels also depended on not only starch concentration, but also the properties of starch: gelatinization and/or swelling ability.

Conclusions

Effects of starch on the texture of surimi-starch gels depended on its concentration, modification, and the ratio of amylose and amylopectin. The lower starch concentration in surimi increased gel strength more effectively than the higher starch concentration. Modification caused the granule to swell easily and resulted in an increase of gel strength, because it caused the internal structure of the granule to become weaker and reduced GT. The amylopectin component made the granule swell and greatly increased gel strength, while the starch with higher amylose decreased gel strength. The influence of heating temperature on the texture depended on the gelatinization properties of the individual starch. Therefore, for native starches, a heating temperature of 90°C was more effective in increasing gel strength than a heating temperature of 70°C, especially CS. For modified starches, heating temperatures did not affect gel strength because their internal structure was different from native starches and the granules could swell at lower

temperature. A longer heating time slightly increased the gel strength of surimi-starch gels. Shear strain was not affected by heating temperature and time, but greatly decreased when starch granules could not absorb enough water, such as CS. From microstructure of the gels, the larger the size of starch granule resulted in the stronger gel and indicated that the more pressure from the granule was given into the gel matrix. Higher heating temperature caused granules to become bigger for native starches, but did not affect modified starches. The color of surimi-starch gel depended on not only the starch concentration but also the starch properties. If the granules were not fully swollen in the gel, the gel became more opaque (higher L* value) and slightly more yellow (higher b* value) as the starch concentration increased. If the granules were swollen in the gel, the gel became more translucent (lower L* value) and slightly blue (negative b* value).

Chapter 4

Stress Relaxation Studies on Surimi-Starch Gels

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Abstract

The viscoelastic properties of surimi-starch gels were determined by stress relaxation experiments from uniaxial compressive test, in order to evaluate effects of starch as well as heating temperature and time on surimi-starch gel structure. Heating surimi paste at higher temperature (90°C) for longer heating time (up to 60 min) did not change the viscoelastic properties of surimi gels. It was shown that 70°C for 20 min was good enough to form a three dimensional structure of gels. When starch was added into surimi, the viscoelastic properties of surimi-starch gels were changed by its type and concentration. All gels showed a typical behavior of viscoelastic solid due to a dominant role of covalent bonds and reinforcement of starch granules in surimi-starch gels.

Key word: stress relaxation, viscoelasticity, surimi, and starch.

Introduction

Fish myofibrillar proteins form a three-dimensional network structure upon thermal treatment. Such network structure can exhibit specific mechanical behaviors and is often used as a target for quality control. Normally the mechanical behaviors of foods are time-dependent (Mohsenin, 1986). Therefore, in order to characterize the mechanical behaviors of surimi gels, the concept of viscoelasticity, such as viscous and elastic properties, is applied. Like most other gel-type foods, surimi gel displays viscoelastic properties due to its structural conformation (Hamann and MacDonald, 1992). The fundamental tests can be used to directly evaluate the viscoelastic properties of surimi gels to understand structure-function relationships in surimi seafoods. While torsion test is widely used to measure the fractural properties of surimi gels, non-fractural analysis has became important to determine time/temperature history of gels. Thermal scanning rigidity monitor was often used to continuously evaluate the changes of rigidity modulus and energy loss (energy damping) of surimi from sol to gel during thermal processing (Montejano et al., 1984). In recent years, dynamic test is more frequently used to measure the viscoelastic properties of surimi gels (Hamada and Inamasu, 1983, Ma et al., 1996).

Stress relaxation, a non-fractural (small-strain) fundamental test, is frequently used to investigate viscoelastic behaviors of surimi gels (Hamann and MacDonald, 1992; Ma et al., 1996). In stress relaxation test, the sample is suddenly brought to a given

deformation. During the holding at such constant deformation, the decay of stress is measured as a function of time. Surimi gel is an intermediate form between a solid and a liquid exhibiting both elastic and viscous properties (Oakenfull, 1987; Hamann and MacDonald, 1992). Unlike most of foods, surimi seafoods are homogeneous and isotropic materials. Therefore, when stress relaxation test is applied, the qualitative comparisons can be made between curves obtained with the same conditions and facilitate interpretating the structure of the sample.

Starch is widely used to improve or modify the quality of surimi seafoods. Large deformation (fracture) methods, such as torsional test, are commonly used for the study of the texture of surimi-starch gels. However, few studies of small deformation (non-fracture) using stress relaxation have been applied to investigate the viscoelastic properties of surimi-starch gels. The objective of this study was to investigate effects of different starches and their concentrations, as well as heating temperature and time on the viscoelastic properties of surimi-starch gels under stress relaxation test.

Materials and Methods

Materials

Frozen Alaska pollock (*Theragra chalcogramma*) surimi (high grade) was obtained from Trident Seafood Corporation (Seattle, WA), and cut into small blocks (about 1,000

g). Then they were vacuum-packaged and kept in a freezer (-25°C). Native and modified starches were used for the experiments: potato starch (PS) and modified potato starch (MPS) with acetylation were obtained from Roquette America, Inc. (Keokuk, IA); corn starch (CS) and two modified waxy maize starches (MWMS-I and II) were obtained from Cerestar (formerly American Maize-Products Company, Hammond, IN). MWMS-I was all amylopectin (100%) and modified with adipation and cross-linking. MWMS-II was hydroxypropylated and contained amylose (45%) and amylopectin (55%).

Gel preparation

Surimi block was tempered at room temperature (25°C) for 2 hr before mixed with other ingredients. Chopping was performed as described by Park et al. (1997). During chopping, 0, 3, 6, and 9% starch concentrations were added into surimi and mixed thoroughly for additional 4 min, while the moisture maintained 78%. Paste was then stuffed into the stainless tubes (inner diameter = 1.9 cm). Surimi paste was heated in a water bath (70° and 90°C for 20 min) to measure the effect of heating temperature. In addition, surimi paste was heated at 90°C for various heating times (10, 20, 40, and 60 min) to measure the effect of heating time. Surimi-starch samples were heated at 90°C for 20 min to determine the effect of starch. After heating, the samples were rapidly cooled down in the ice-water, and then kept in a refrigerator overnight (5°C).

Stress relaxation test

Before testing the sample, gels were kept at room temperature (20 - 25°C) for 2 hr, and then cut into a cylindrical shape (diameter = 1.9 cm and length = 1.9 cm). Stress relaxation tests were performed using an MTS Sintech (MTS System Corporation, Cary, NC). Gel cylinders were instantaneously compressed into constant strain level (10%) at cross-head speed of 10 cm/min using a 100 lb loadcell. Such deformation (strain) was held to measure stress relaxation for 30 min at room temperature (20-25°C). The compressive stress-time data were recorded and stored in a computer equipped with MTS Sintech.

Stress relaxation curves were constructed by plotting stress vs. time (Fig. 4.1). Initial stress (σ_0) and equilibrium stress (σ_e) were obtained directly from the relaxation curves. The relaxation time (T_{rel}) is the time for which the stress decays to reach 1/e or 37% of (σ_0-σ_e). However, T_{rel} can indicate the ratio of viscous component and elastic component, namely, the viscoelastic properties of the gel (Mohsenin, 1986). For ideal elastic materials, all the energy is converted in the deformation and stored in the solid, so there is no relaxation or $T_{rel} = \infty$ and $\sigma_0 = \sigma_e$. For ideal viscous materials, any stress can not be maintained in the absence of motion and all the energy is totally dissipated due to the motion of the liquid, so the stress will be relaxed immediately or $T_{rel} = 0$ and $\sigma_0 = 0$. The response of a viscoelastic material lies between those two extremes: some of energy is stored due to the solid part of the system while the rest is dissipated due to the liquid part. Therefore, the longer the relaxation time, the slower the force decayed, and

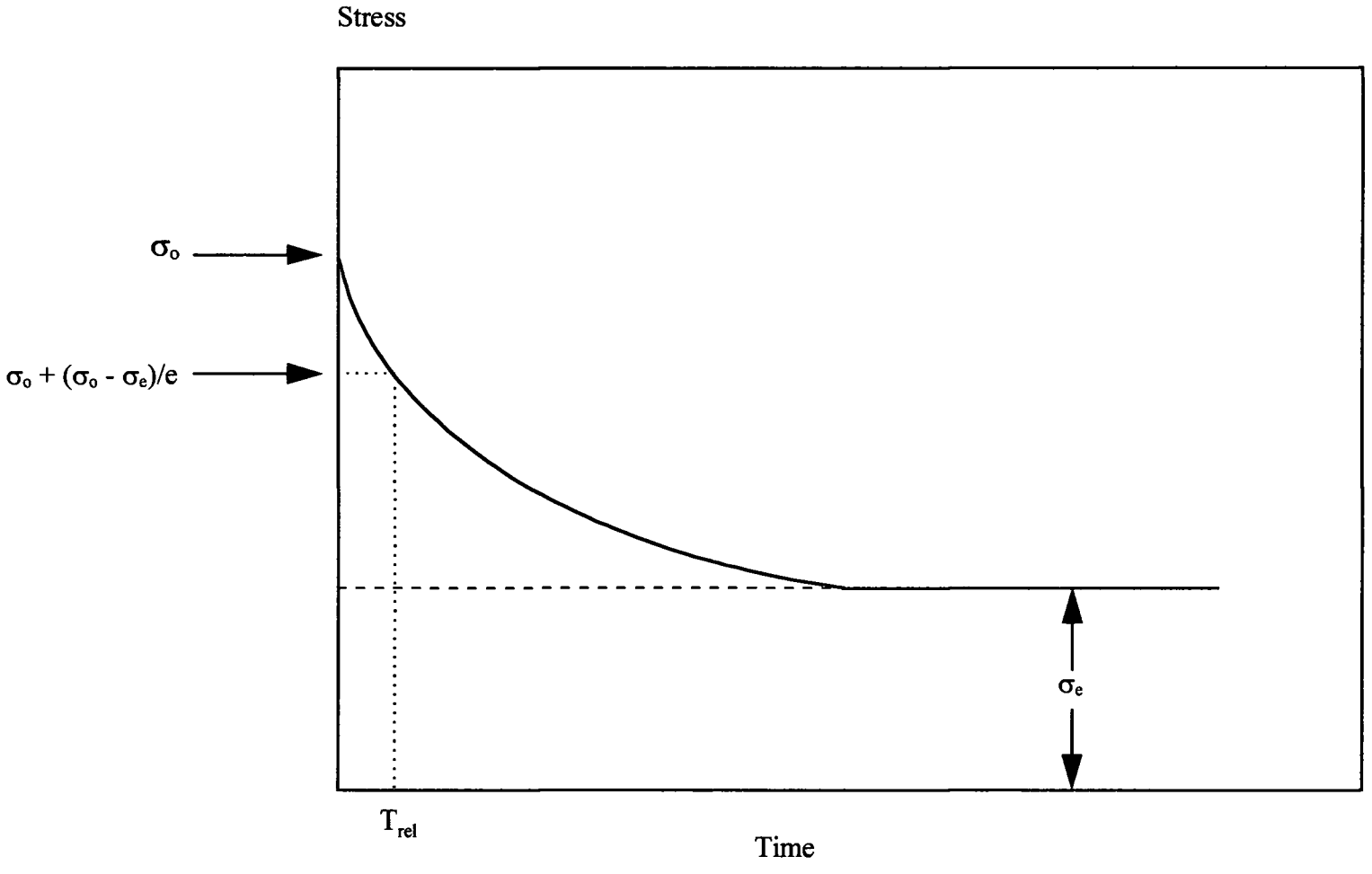

Figure 4.1. Relationship between stress and time in stress relaxation curve.

the more elastic the gel. Equilibrium stress (σ_e) indicates the inherent elastic property of a viscoelastic material (Liu and Foegeding, 1996). The change of those parameters can facilitate the effects of processing conditions (heating temperature and time) and ingredients on structure of surimi-starch gels.

Statistical analysis

For each treatment, three replicates were used. ANOVA test was used to analyze the data. The least significant difference (LSD) was used to compare treatment means at $P<0.05$. All statistical analyses were performed using Statgraphics Version. 6.0 (Manugistics, Rockville, MD).

Results and Discussions

The results of stress relaxation of two surimi gels, prepared at 70° and 90°C for 20 min, were not different ($P>0.05$) (Fig. 4.2). σ_0, σ_e, and T_{rel} were 1382 Pa, 452 Pa, and 35.5 s for gels prepared at 70°C, and σ_0, σ_e, and T_{rel} were 1285 Pa, 440 Pa, and 42.6 s for gels prepared at 90°C, respectively. It demonstrated that there was no different effect due to heating temperatures on final viscoelastic properties of surimi gels. In other words, fish myofibrillar proteins (surimi) could complete their gelation at 70°C for 20 min. Especially when salt was added during the mixing or chopping, the denaturation temperature of fish myosin and actin significantly decreased (Park and Lanier, 1989).

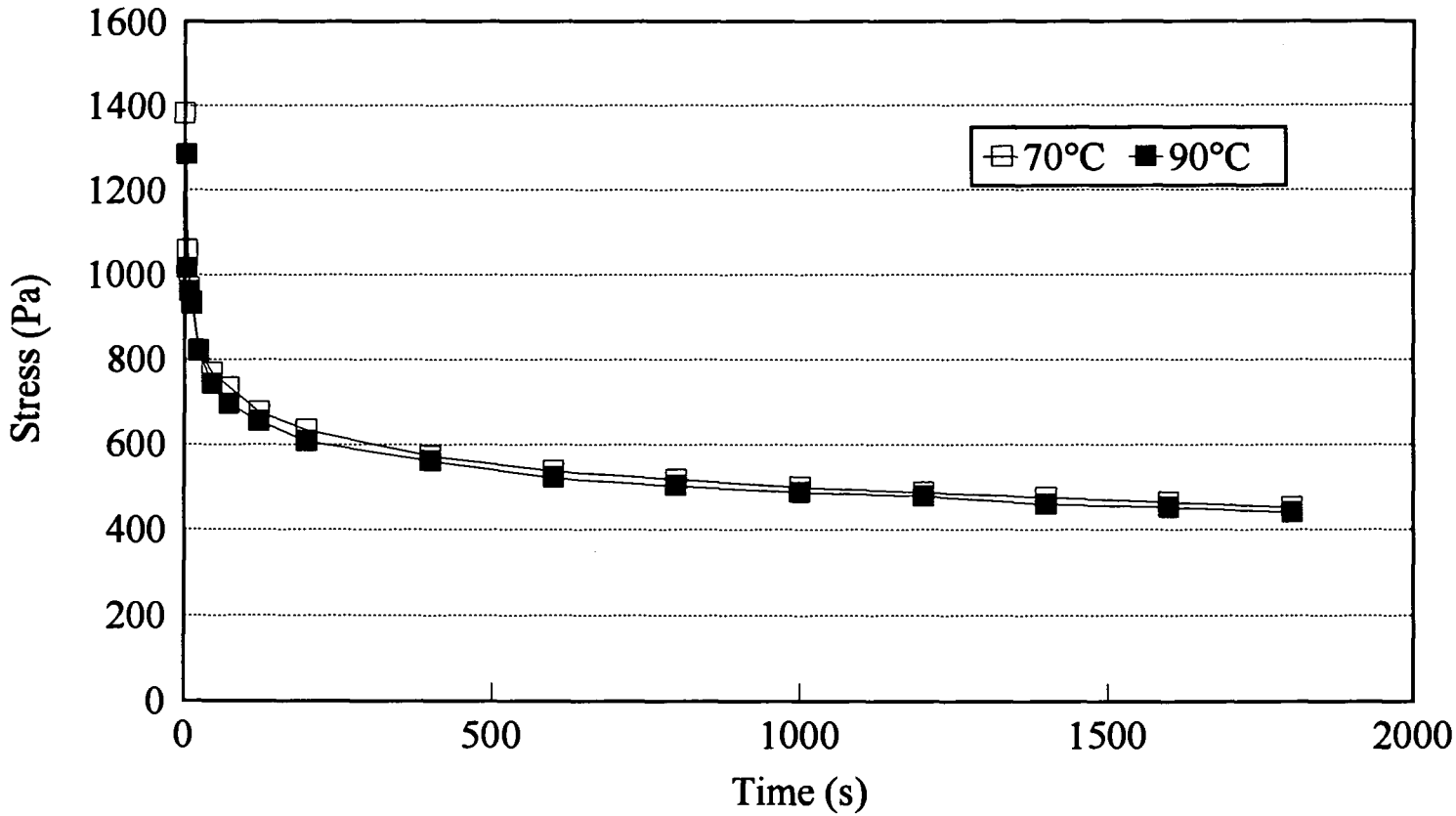

Figure 4.2 Effects of heating temperatures on stress relaxation of surimi gels cooked for 20 min.

Thus three-dimensional structure of surimi gels could be formed at lower heating temperature. According to Peleg (1979), surimi gels were viscoelastic solid, because the stress did not decrease after equilibrium stress was reached due to a part of energy stored.

The results of stress relaxation of four surimi gels, heated at 90°C for 10, 20, 40, and 60 min, were not different ($P>0.05$) in σ_0, σ_e, and T_{rel} (Table 4.1, Fig. 4.3). The effect of heating time on final viscoelastic properties of surimi gels was not observed when the gels were heated at 90°C beyond 10 min. It was probably because gel formation completed within 10 min at 90°C. Consequently, the viscoelastic properties of surimi gels were insensitive to heating temperatures and times once three-dimensional network structure of gels was formed.

Table 4.1. Effect of heating time at 90°C on viscoelastic properties of surimi gels.

Heating time (min)	10	20	40	60
Initial stress (Pa)	1278[a]	1285[a]	1285[a]	1216[a]
Equilibrium stress (Pa)	409[a]	440[a]	409[a]	382[a]
Relaxation time (s)	48.2[a]	42.6[a]	47.9[a]	50.9[a]

[a] Means in the same row followed by different letters are significantly different ($P<0.05$).

When surimi proteins mixed with different starches were heated at 90°C for 20 min, the curves of stress relaxation of all gels also showed a typical viscoelastic solid (Fig. 4.4). There were differences for σ_0, σ_e, and T_{rel} ($P<0.05$) among different starches and starch concentrations. For MPS, CS and MWMS-I, T_{rel} increased, the degree of the

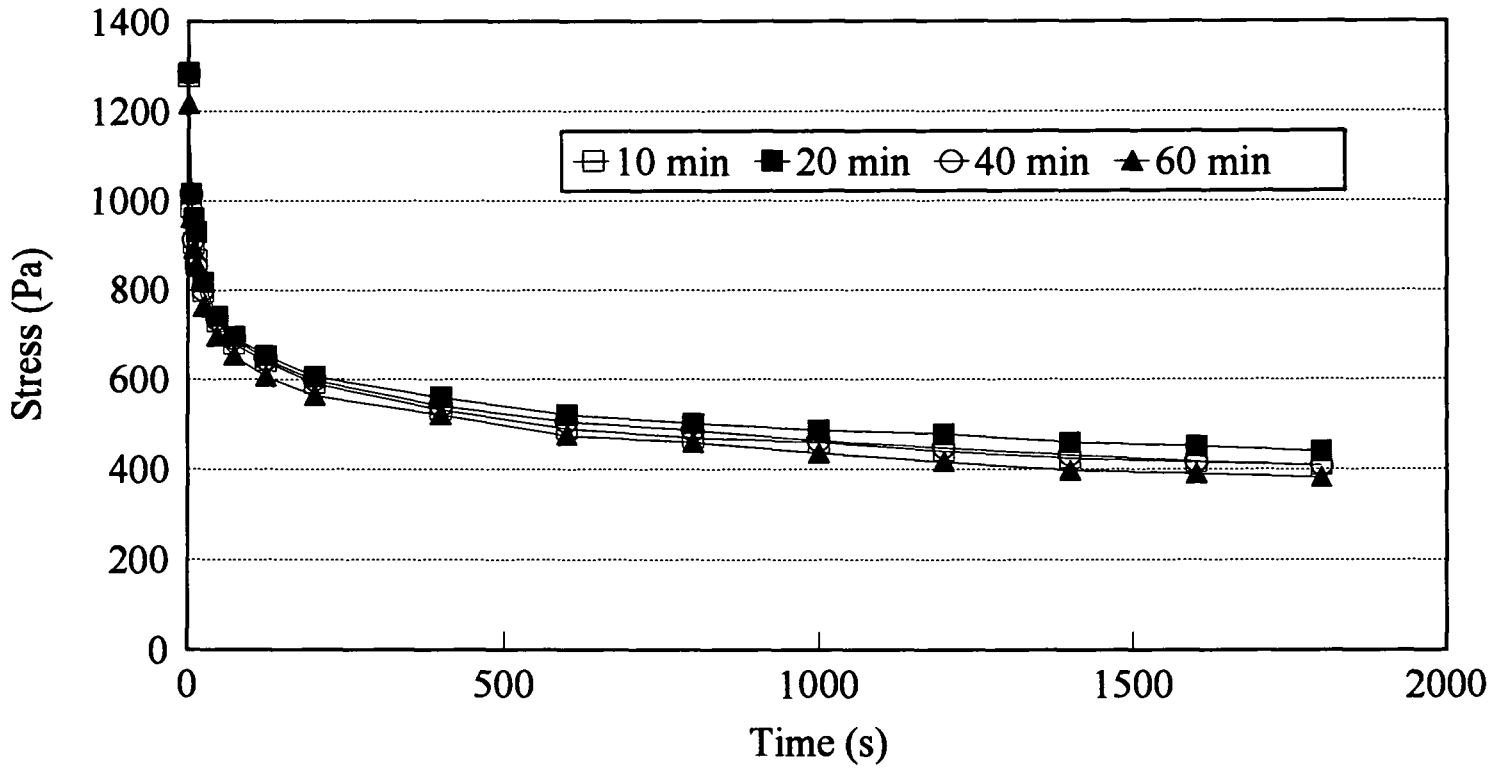

Figure 4.3. Effect of heating times on stress relaxation of surimi gels cooked at 90°C.

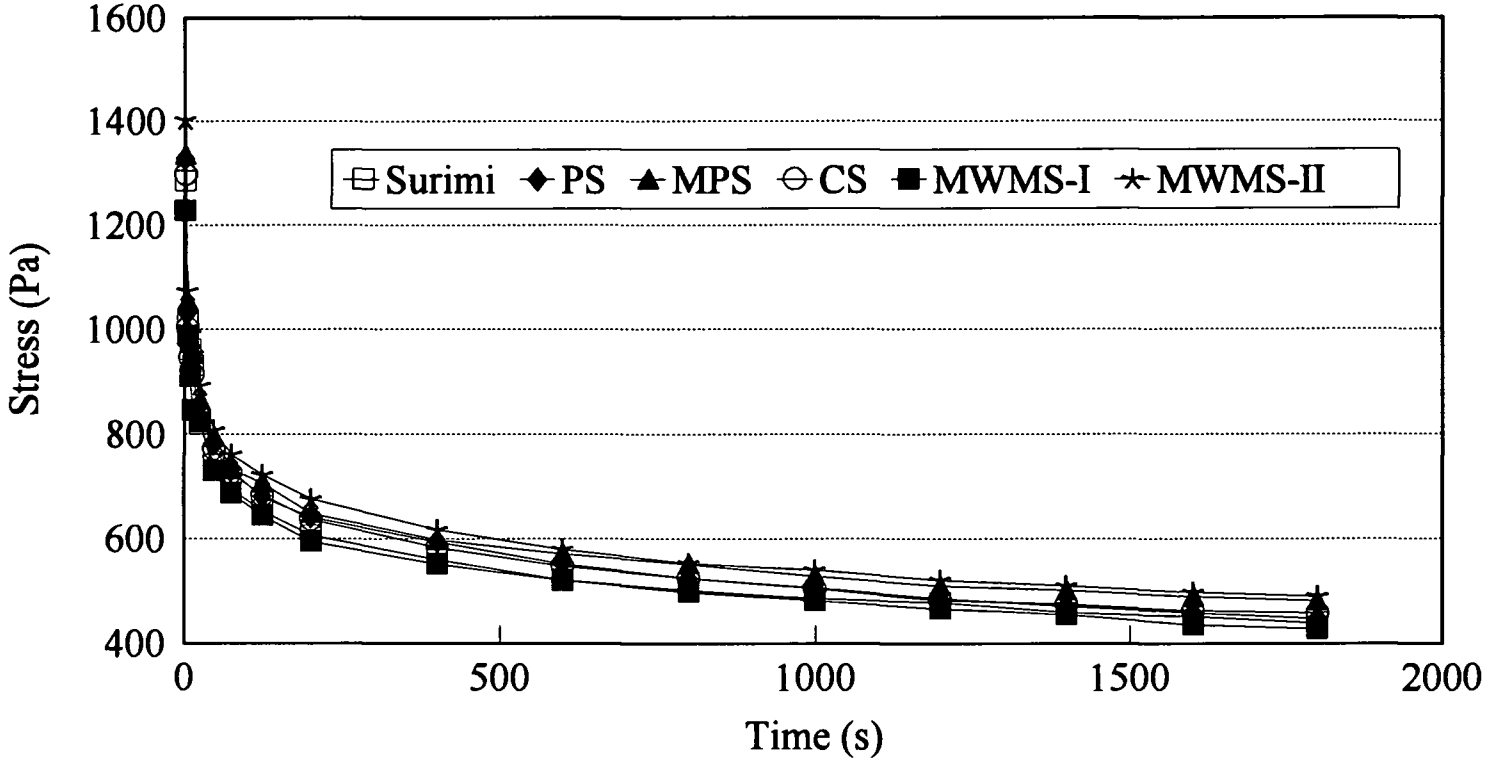

Figure 4.4. Effect of various starches (3%) on stress relaxation of surimi-starch gels (90°C for 20 min).

decay decreased, and the gel became relatively more elastic (Fig. 4.5). For PS, T_{rel} increased at 3% and then decreased as its concentration increased further. Thus at the higher concentration of PS, the degree of the decay increased, and the gel became relatively more viscous. For MWMS-II, T_{rel} was remained constant up to the level of 6% and then decreased at 9% inclining to be viscous. It is well known that the cross-linkings among polymer-polymer and polymer-solvent combined with the fluidity of the immobilized solvent give gels the viscoelastic properties (Schmidt, 1981). In surimi gels, there are four kinds of linkages in the system. They are non-covalent bonds (hydrogen bond, salt linkage, and hydrophobic bond) and covalent bond (disulfide bond) (Niwa, 1992). Recently another non-disulfide covalent bond, ε-(γ-glutamyl)-lysine bond, is observed in the surimi gel (An et al., 1996). Those bonds contributed to stabilize the gel structure and the viscoelastic properties of surimi gels. Those bonds have different properties in the gels. The non-covalent bonds are labile cross-links and the covalent bonds are permanent cross-links (Diefes et al., 1993; Hamann and MacDonald, 1992; Masi and Addeo, 1986). In the surimi-starch system, the viscoelastic properties could probably be influenced by those weak and strong bonds. Hydrogen bond plays one of major roles in stabilizing the gel structure and is related to water immobilization (Niwa, 1992). The starch granules could thermally absorb water, and attach the water by hydrogen bond upon cooling. When starch was added into surimi, the water could be redistributed between protein and starch during thermal processing. Because the starch granules absorbed water from surroundings in the surimi-starch system, the available water for protein could be limited when starch was introduced. Such redistribution of the

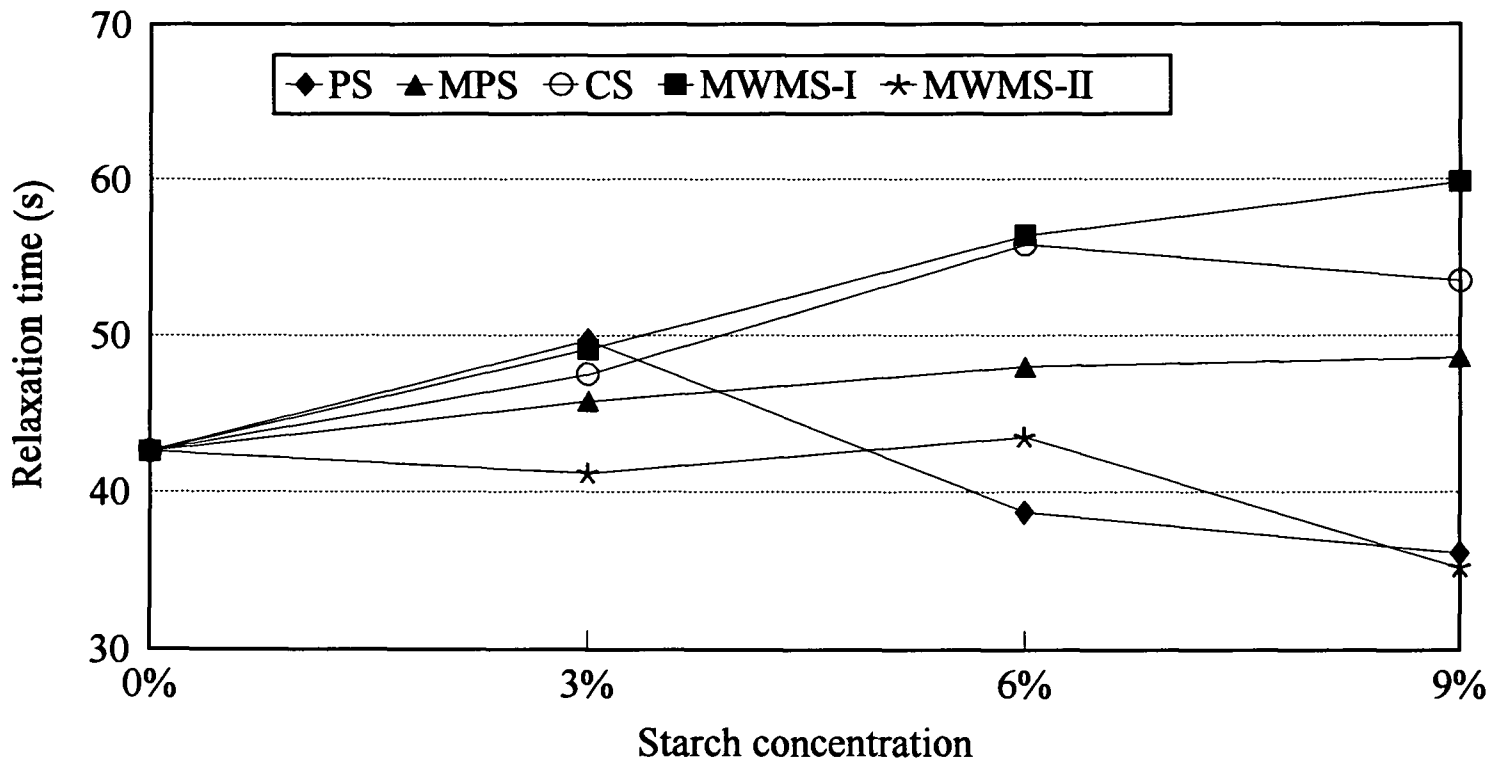

Figure 4.5. Effect of various starches on relaxation time of surimi-starch gels (90°C for 20 min).

water changed the linkages between water and protein (hydrogen bonds). The influence of hydrophobic bonds and covalent bonds depended on the concentration of hydrophobic amino acids and cysteines in fish proteins, respectively (Niwa, 1992). When starch was added into surimi and the moisture content was maintained constant, the concentration of fish proteins decreased. The influences of hydrophobic bonds and covalent bonds on surimi-starch gel structure decreased. Thus effects of covalent bonds and non-covalent bonds were changed in surimi-starch gels, resulting in the change of the viscoelastic properties of the gels. Consequently, the viscoelastic properties of surimi-starch gel were influenced by starch concentrations and botanical sources. According to Mohsenin (1986), T_{rel} represents the ratio of viscous and elastic component. As starch concentration increased, the gels became more elastic with MPS, CS, and MWMS-I and more viscous with PS and MWMS-II (Fig. 4.5).

Initial stress (σ_0) was increased at low starch concentration (3%), and then greatly decreased at high concentration (9%) ($P<0.05$) (Fig. 4.6), except CS. When the constant deformation is applied to the gel, it takes a finite amount of energy to disturb the network of the gel, resulting in breaking and deforming of weak bonds (Diefes et al., 1993; Hamann and MacDonald, 1992; Masi and Addeo, 1986). Thus initial elastic component or stress might be attributed to the undisturbed protein network, which could represent the comprehensive properties of all bonds (covalent and non-covalent bonds) in the gels. When starch was added into surimi, initial stress was changed depending on the starch concentrations (Fig. 4.6). It demonstrated that the viscoelastic properties of surimi-starch

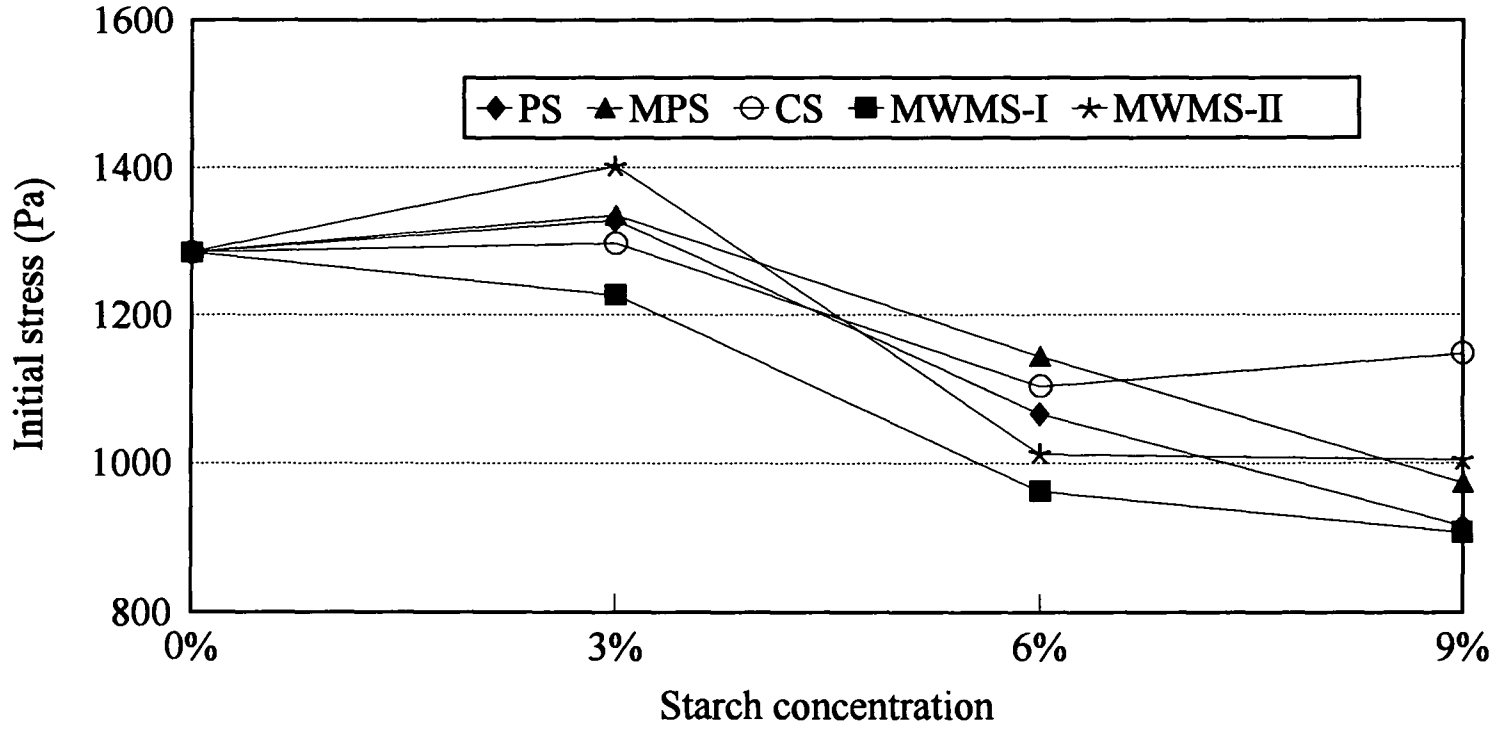

Figure 4.6. Effect of various starches on initial stress of surimi-starch gels (90°C for 20 min).

gels were different from that of surimi gels. Because weak bonds were broken and deformed, the decay of stress occurred.

Equilibrium or un-relaxed stress (σ_e) slightly increased when 3% starch (PS, MPS, CS and MWMS-II) was incorporated and did not change with MWMS-I (Fig. 4.7). Equilibrium stress decreased when 6% or 9% starch was added ($P<0.05$), except CS (Fig. 4.7). Since the weak bonds (non-covalent bonds) are broken easily by the external force, initial stress can decrease very rapidly (McEvoy et al., 1985). However, the weak bonds may possibly be reformed at new condition in deforming gels and contribute little or none to the stress (Hsieh and Regenstein, 1992). Equilibrium stress is independent of time and caused by the remaining covalent bonds (Hsieh and Regenstein, 1992; Ziegler and Rizvi, 1989), because the covalent bond (330-380 kJ/mol) is not broken as easily as hydrogen bond (8-14 kJ/mol), hydrophobic interaction (4-12 kJ/mol) and salt linkage (42-84 kJ/mol) (Cheftel et al., 1985). Polyacrylamide gels, which are formed exclusively by covalent bonds, exhibit no stress relaxation (Foegeding et al., 1994). The covalent bond can indicate the inherent elastic property of a viscoelastic material (Liu and Foegeding, 1996), and is one of the most important bonds to contribute to the gel structure of fish proteins. The concentration of covalent bonds is dependent on the concentration of proteins. When starch was added into surimi, the concentration of fish proteins in the surimi-starch system decreased. Thus, the concentration of covalent bonds among fish proteins could be decreased so that the contribution of covalent bonds to the network was reduced. It was impossible that covalent bonds could be formed between fish proteins and carbohydrates.

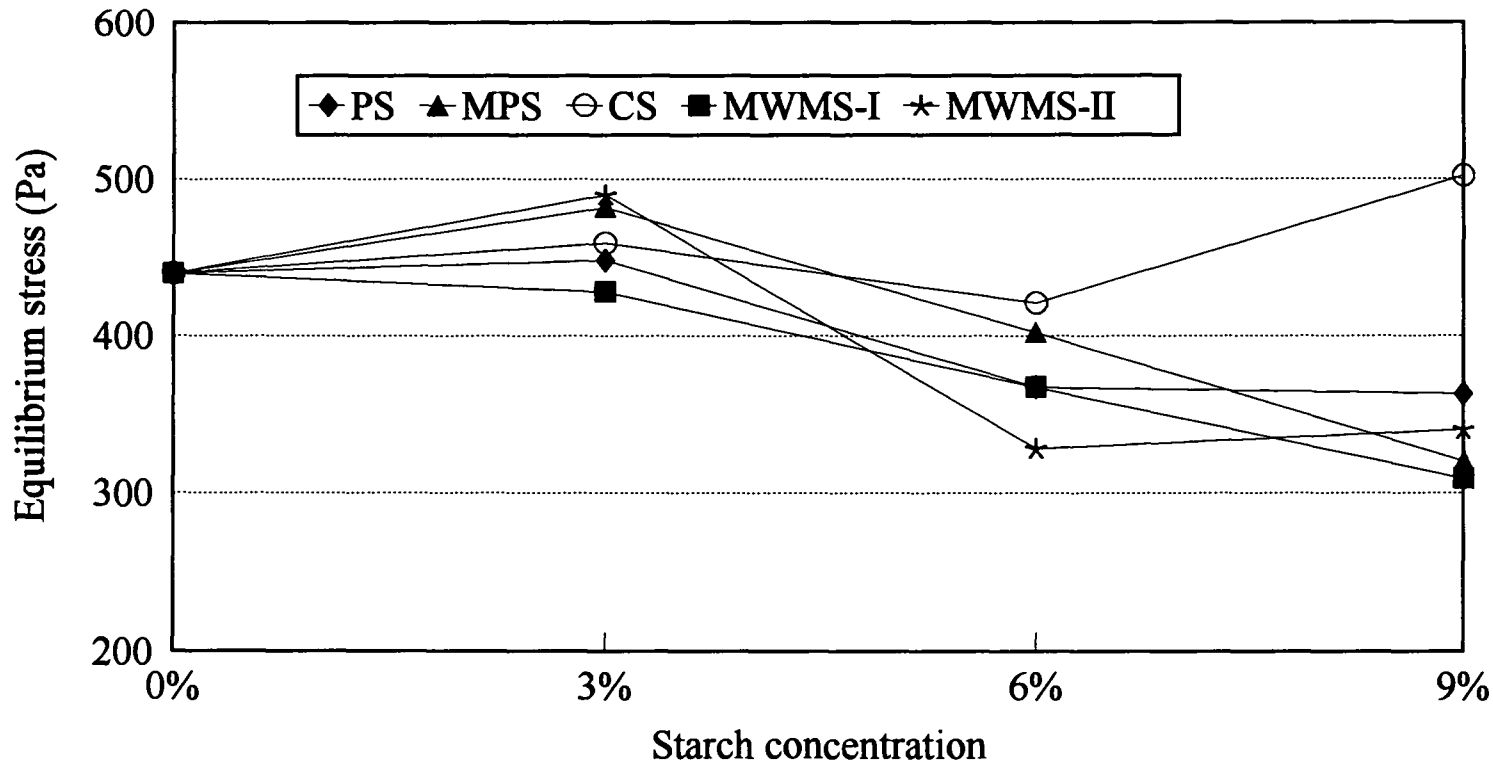

Figure 4.7. Effect of various starches on equilibrium stress of surimi-starch gels (90°C for 20 min).

However, equilibrium stress, which is thought to be caused by the covalent bonds, actually increased with 3% starch of PS, MPS, CS and MWMS-II and did not change with MWMS-I. Equilibrium stress decreased when extra starch (6% or 9%) was added (Fig. 4.7). It indicated that surimi-starch gels became more rigid and less fluid at 3%, and became less rigid and more fluid at 6% and 9%. The addition of starch was probably attributed for the reduced covalent bonds. As starch granules absorbed water from the surimi-starch system, the concentration of fish proteins at the low starch concentration increased in the continuous phase (Lanier, 1991) because water was partitioned into the swollen starch granule. However, swollen granules could not increase the concentration of disulfide bonds in surimi-starch gels resulting in the change of equilibrium stress. As the starch granules were enlarged in the gel during heating, the granules could also cause the pressure in the gel matrix (Lee et al., 1992). Such reinforcement could probably cause the increased or unchanged equilibrium stress. At the high starch concentration (6% or 9%), as the concentration of fish proteins was relatively diluted so much that the reinforcement from swollen starch granules could not be remained. Therefore, low equilibrium stress was obtained, especially with 9% starch (except CS). The starch could increase or maintain the elasticity of surimi gels at its low concentration (3%). The reinforcement of starch granules in surimi-starch gels was shown by the values of equilibrium stress.

The reduction of initial stress upon the addition of starch was more than that of equilibrium stress (Fig. 4.6 and Fig. 4.7). The decay of stress, which is a difference

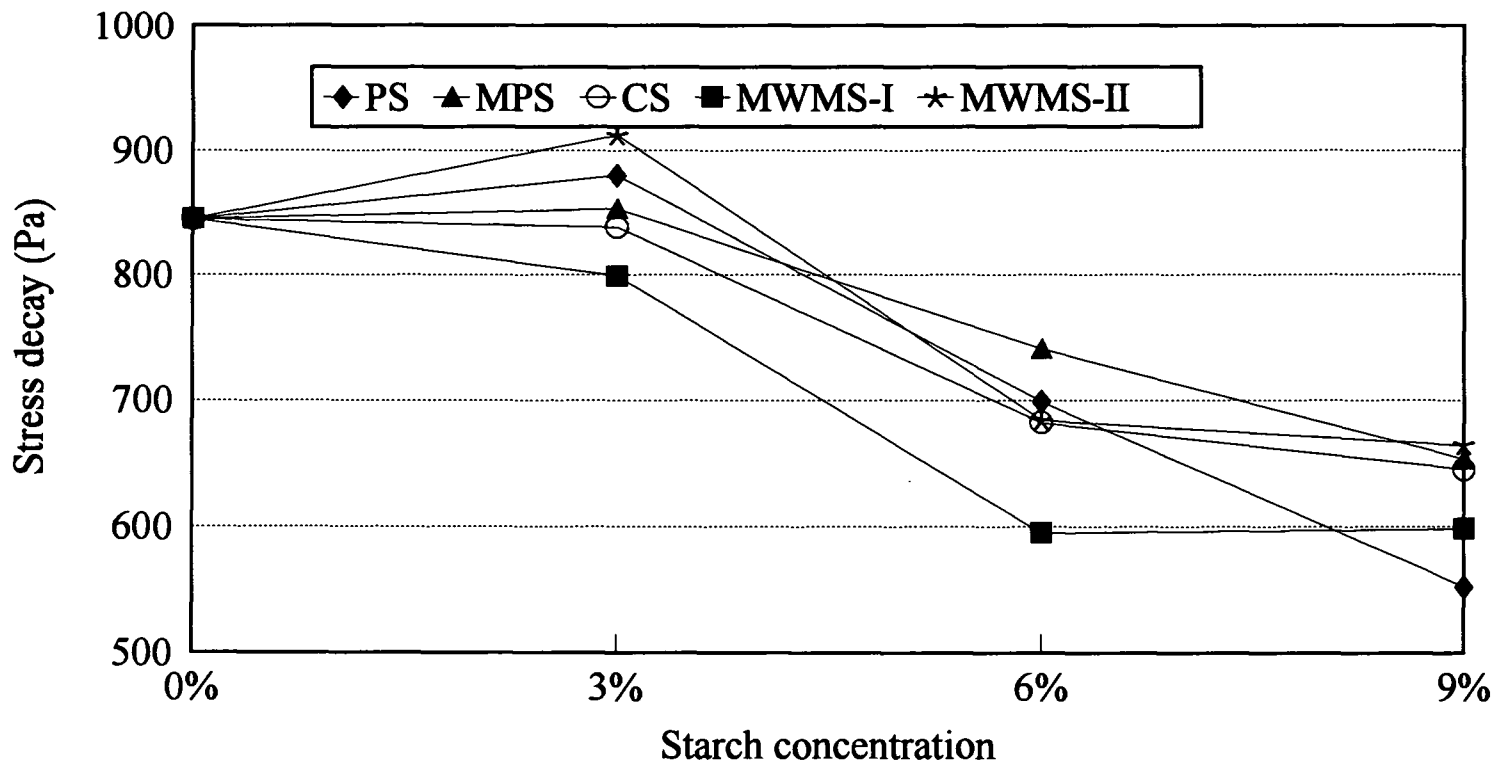

Figure 4.8. Effect of various starches on stress decay of surimi-starch gels (90°C for 20 min).

between initial stress and equilibrium stress (σ_0-σ_e), increased at 3% starch and then greatly decreased when 6% or 9% starch was added (Fig. 4.8). Because initial stress represented the properties of all bonds involved in the gels and equilibrium stress represented the properties of covalent bonds in the gels, the decay of stress could indicate the properties of weak or labile bonds in the gels. When an external force was applied to the gel, those labile bonds were broken or deformed, resulting the decay of stress. The addition of water along with starch to surimi could increase the effect of hydrogen bonds in surimi-starch gel structure, because the hydroxyl hydrogens or oxygens of starch can potentially bind water (Whistler and Daniel, 1985). In fact, the effect of hydrophobic bonds could be decreased, due to the reduced concentration of fish proteins. Thus it was shown that the decay of stress of the gels was increased or was remained constant at 3% starch (Fig. 4.8). When the starch concentration increased further, the concentration of fish proteins decreased so that the decay of stress decreased.

Conclusions

Stress relaxation test, as a non-fracture analysis, was effective to determine the viscoelastic properties of surimi gels with or without starches as affected by various thermal conditions. Heating surimi paste at higher temperature (90°C) for longer heating time (up to 60 min) did not change the viscoelastic properties of surimi gels. This observation confirmed that 70°C for 20 min was good enough to form a three dimensional

structure of gels. When starch was added into surimi, the viscoelastic properties of surimi-starch gels were changed by the type and the concentration of starch. All gels showed a typical behavior of viscoelastic solid due to a dominant role of covalent bonds and reinforcement of starch granules in surimi-starch gels.

Chapter 5 Summary

The starch, one of most important ingredients in surimi seafood, influenced rheological, microstructural, and color properties of the product. Effects of the starch on the texture of surimi-starch gel depended on its concentration, modification, and the ratio of amylose and amylopectin. The low starch concentration in surimi paste increased the gel strength more effectively than the high starch concentration. Modification, causing the weaker internal structure of the granule and the reduced GT, induced the granule to swell easily and resulted in the increased gel strength. Amylopectin component facilitated the granules swelling more and greatly increased the gel strength, while the starch with high amylose slightly decreased the gel strength. The influence of heating temperature on the texture depended on the gelatinization properties of the individual starch. Therefore, for native starches, high heating temperature (90°C) was more effective to increase the gel strength than low heating temperature (70°C), especially with CS. For modified starches, heating temperature did not affect the gel strength because their internal structure was different from native starches and the granules could swell at low temperatures. A longer heating time slightly increased the gel strength of surimi-starch gel. Shear strain was not affected by heating temperature and time, but greatly decreased when the higher concentration of starch (especially CS) was introduced due to most of granules unswollen.

The size of the starch granules, under microstructural evaluation, was closely related to the textural properties of surimi-starch gels. It showed that high heating temperature caused native starch granules to become larger but did not affect modified starch granule.

The color of surimi-starch gels depended on not only starch concentration but also the properties of starch. When the granules were not fully swollen in the gel, the gel became more opaque (higher L* value) and slightly increased b* value as starch concentration increased. When the granules were fully swollen in the gels, the gels became more translucent (lower L* value) and slightly decreased b* value.

Stress relaxation test revealed that the viscoelastic properties of surimi-starch gels could be measured without fracturing gels. Once three dimensional network structure of myofibrillar proteins was formed, additional thermal treatments did not influence the viscoelastic properties of surimi gels. When starch was added into surimi, the viscoelastic properties of surimi-starch gels were changed by the type and concentration of starch. All gels showed a typical behavior of viscoelastic solid due to a dominant role of covalent bonds and reinforcement of starch granules in surimi-starch gels.

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Appendix

Preparation of Temperature-Tolerant Fish Protein Gels Using Special Starches

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Abstract

For temperature-tolerant surimi starch gels, ARD 2683 and 810 Stabilizer were the most effective at a level of 1% and 2%, respectively. Versa Gel maintained textural strength up to 8% in both warm and cold serving temperatures, which could replace 36% surimi as well as resulting in great economic savings. Expressible moisture, commonly known as drip loss, can be significantly minimized during frozen storage when ARD 2683, 2684, and 810 Stabilizer were used. Textural stability of frozen surimi-starch gels were consistently maintained with 810 Stabilizer and Versa Gel, and slightly less effective with ARD 2683 and 2684. During frozen storage L* and b* continued to decrease with a starch content up to 4%. There was no significant difference in color properties between starches, except PFP. According to a consumer taste panel for surimi-based crabmeat, the product with Versa Gel was preferred for warm serving and 810 Stabilizer for cold serving.

Introduction

Since the early 1980s, surimi-based seafood consumption in the United States has increased from ~3 million to 160 million lb. Surimi, mechanically deboned washed and cryostabilized fish proteins, is widely used as an ingredient for a variety of surimi seafood products, including crabmeat analogs, kamaboko, and fish sausage. Starch is one of the most important ingredients to formulate surimi-based seafoods. It is used to strengthen textural properties, increase freeze-thaw stability of the product, and decrease the cost while still maintaining the desired quality of the product (Kim and Lee, 1987). During thermal gelation of surimi protein, the gelatinization of starch granules occurs, but is delayed by salt and sucrose (Wu et al., 1985a). Starch granules fill the interstitial spaces of the gel network, swell in water surrounding the protein matrix, and expand themselves until the granules are confined by the matrix resulting in a cohesive, firm gel structure (Lee and Kim, 1986a; Okada and Yamazaki, 1959).

Surimi-based products are commonly marketed as frozen in the United States. Therefore, freeze-thaw stability is an important characteristic of products. Surimi-based seafoods containing an unmodified starch, especially potato starch which can greatly strengthen the texture of gels, but has poor freeze/thaw stability during long-term frozen storage (Okada, 1986). The product becomes brittle and wet with extended storage due to retrogradation of gelatinized starch. However, waxy starches retain much better freeze/thaw stability in frozen food than starches that contain large amounts of amylose

(Whistler and Daniel, 1985). This is because the waxy maize starch naturally contains ~100% branched chain amylopectin. The large, branched chain of amylopectin minimizes the mobility of polymers and interferes with any tendency for them to align; namely, they cannot orient closely enough to form significant hydrogen bondings. Based on these properties, waxy maize starch could have outstanding characteristics to become a superior ingredient for surimi-based seafoods. However, no attempts have been made to investigate an optimum level based on the application of products.

For consumers, temperature of surimi-based products at serving is one very important factor affecting the texture (Howe et al., 1994). The surimi-based products are largely served cold, but sometimes served at warm applications. In the past, experiments to investigate the effects of starch on surimi gels were conducted at room temperature without consideration of serving temperatures. With the exception of recent studies (Howe et al., 1994; Park, 1995a), few attempts have been made to determine textural characteristics of surimi-starch gels at different test temperatures.

Objectives of this study were: (1) to investigate the effect of selected starches on gel functional properties as affected by different test temperature (5° and 50°C); (2) to evaluate the effects of refrigerated storage on textural properties; (3) to investigate the effects of frozen storage on textural properties, color and expressible moisture; and (4) to develop temperature-tolerant surimi-based crabmeat according to consumer taste panel results.

Materials and Methods

High grade (FA) Alaska pollock (*Theragra chalcogramma*) surimi, was obtained from Oceantrawl Inc. (Seattle, WA). Surimi was cut into about 1,000g blocks and kept in a freezer (-25°C) throughout the experiments. Surimi contained 4% sugar, 5% sorbitol, and 0.3% sodium tripolyphosphate as cryoprotectants. Six starch samples were obtained from American Maize-Products Company (Hammond, IN). They were native corn starch (PFP) and five modified starches (Amerimaize 2245, ARD 2684, ARD 2683, 810 Stabilizer, and Versa Gel) as shown in Table A.1.

Table A.1 Experimental Starches

Starch	Amylose(%)	Amylopectin (%)	Modification
PFP (corn starch)	25	75	None
ARD 2684	0	100	PO-treated[1] (4.0%)
ARD 2683	0	100	PO-treated (4-4.5%), Duwx[2]
Amerimaize 2245	0	100	PO-treated,X-linked[3],Duwx
810 Stabilizer	25	75	PO-treated (3.5-4.5%)
Versa Gel	0	100	Adipated, X-linked, Acetylated

1. PO-treated = hydroxypropylated
2. Duwx = dull waxy starch
3. X-linked = cross-linked

Gel Preparation

Six starches were divided into six groups with different levels of starch concentration: 0, 1, 2, 4, 8, 12%, while surimi contents were accordingly adjusted to 80, 76.4, 72.8, 65.6, 51.2, 36.8%, respectively to maintain moisture content at 78%. Frozen surimi was thawed at room temperature for 2 hr and cut into 3-cm cubes. Surimi cubes were placed in a Stephan vacuum cutter (model UM 5 Universal; Stephan Machinery Corp., Columbus, OH). Frozen cubes were chopped at low speed for the 1.5 min. Salt (2%) was sprinkled in and chopped at low speed for 0.5 min. Ice/water with or without starch was added and chopped at low speed for 1 min. Chopping continued at high speed under vacuum of 0.5 kPa for the final 3 min. During chopping, a constant cold temperature (<8°C) was maintained using a circulator (model RET-100LP; NesLab Instruments, Inc., Portsmouth, NH). The paste was stuffed into stainless steel tubes (inner diameter = 1.9 cm, length = 17.5 cm) with stainless steel screwable caps, using a sausage stuffer (Sausage Maker, Buffalo, NY). The interior wall of the tubes was coated with a film of cooking oil spray. The tubes were submerged in a 90°C water bath and cooked for 15 min. Cooked gels were cooled in ice water.

Textural Properties in Different Temperatures

Chilled gels (4°C) were held at room temperature (22-25°C) for 2 hr before torsion testing. Ten gels were milled into a dumbbell geometry (length = 2.9 cm, end diameter = 1.9 cm, and minimum diameter at center = 1 cm). Shear stress and shear strain of samples, at mechanical failure, were measured using a torsion gelometer (Gel Consultants,

Inc., Raleigh, NC) set at 2.5 rpm (NFI, 1991). To test gels, at different temperature, the sample was loaded in the gelometer, placed in the water bath, and held for 3 min before fracture to obtain an equilibrated temperature. A programmable water bath (NesLab Instruments, Inc., Portsmouth, NH) was used to maintain constant temperature (5° and 50°C).

Freeze/Thaw Test

Cyclic freeze/thaw abuse is known as the best method to estimate long term storage stability in a short period of time. Dumbbell-shaped samples for torsion tests and cylindrical samples (diameter = 1.9 cm, length = 2.9 cm) for color and expressible moisture tests were wrapped in plastic film and frozen at -25°C. Gels abused by a repeated cycle of freezing and thawing (0, 3, 6, 9 cycles) were measured at room temperature to investigate the change of textural properties (NFI, 1991), color properties (L*, b*) (Park, 1995b), as well as expressible moisture (EM) (Jauregui et al., 1981).

A Minolta Chroma Meter CR-310 (Minolta Corp., Ramsey, NJ) with a CIE Lab color scale was used to measure the color of gel. Expressible moisture tests were performed as described: the weight of 3 pieces of Whatman #3 (diameter = 125 mm) filter paper (W1) and the weight of filter paper with polyester mesh (PE. 105, type 502, 690 mesh per cm^2, Henry Simon Limited, Stockport, Cheshire, UK) (W2) were measured. All weights were accurately measured to the 3rd decimal place. Sliced surimi 1.5±0.3 g was placed in the center of the polyester mesh and the polyester mesh was put in the middle

of the filter papers. All weights of samples with the filter paper and the polyester mesh (W3) were measured. The sample was placed in a 50 mL polycarbonate tube and centrifuged at 5,600 rpm (Sorvall RC2b, SS34 rotor) at room temperature for 10 min. All samples were measured in triplicate. After centrifugation, the sample was removed from the tube, surimi was removed with the polyester mesh, and the wet filter paper (W4) was immediately weighed .

$$EM\ (\%) = \frac{W4 - W1}{W3 - W2}\ 100\%$$

Consumer Taste Panel

Four batches of commercial test run were made at Kyotaru Oregon (Salem, OR). Three test starches, replaced 2% potato starch (control), were ARD 2683, 810 Stabilizer, and Versa Gel. Sample products with ARD 2683 and 810 Stabilizer were presented along with the control as a cold serving. The control and sample products with ARD 2683, and Versa Gel were presented for warm servings. The paste panel was conducted at the Oregon State Fair using 173 consumers for cold servings and 162 consumers for warm servings. In addition, a "Just Right" scale was used to estimate the optimum textural preference.

Statistical Analysis

All measurements of each treatment were randomly divided into two groups. Averages of all response variables from each group were calculated. The main effects and second-order interaction effects based on a split-plot design were analyzed using ANOVA (Petersen, 1985). The least significant difference (LSD) was used to compare treatment means at $P < 0.05$. All statistical analyses were achieved using Statgraphics version 6.0 (Manugistics, Rockville, MD).

Results and Discussion

Textural Properties of Surimi-Starch Gel at Different Temperatures.

As a function of textural properties, fracture shear stress indicates gel strength and fracture shear strain denotes gel deformability. In Figs. A.1, and A.2, when test temperatures increased from 5 to 50°C, shear stress of the gel (with or without the starch) decreased and shear strain increased. This was in agreement with other previous reports (Howe et al., 1994, Park, 1995a). There are mainly four types of bonds involved in building a network structure during heat-induced gelation of surimi: ionic linkages, hydrogen bonds, hydrophobic interactions, and covalent bonds (Niwa, 1992). Covalent bonds are the most important to stabilize the gel network since the energy is 330-380 kJ/mol (Cheftel et al., 1985), and their effects on shear stress are independent of test temperature (Foegeding et al., 1994). Hydrogen bonds and hydrophobic bonds are

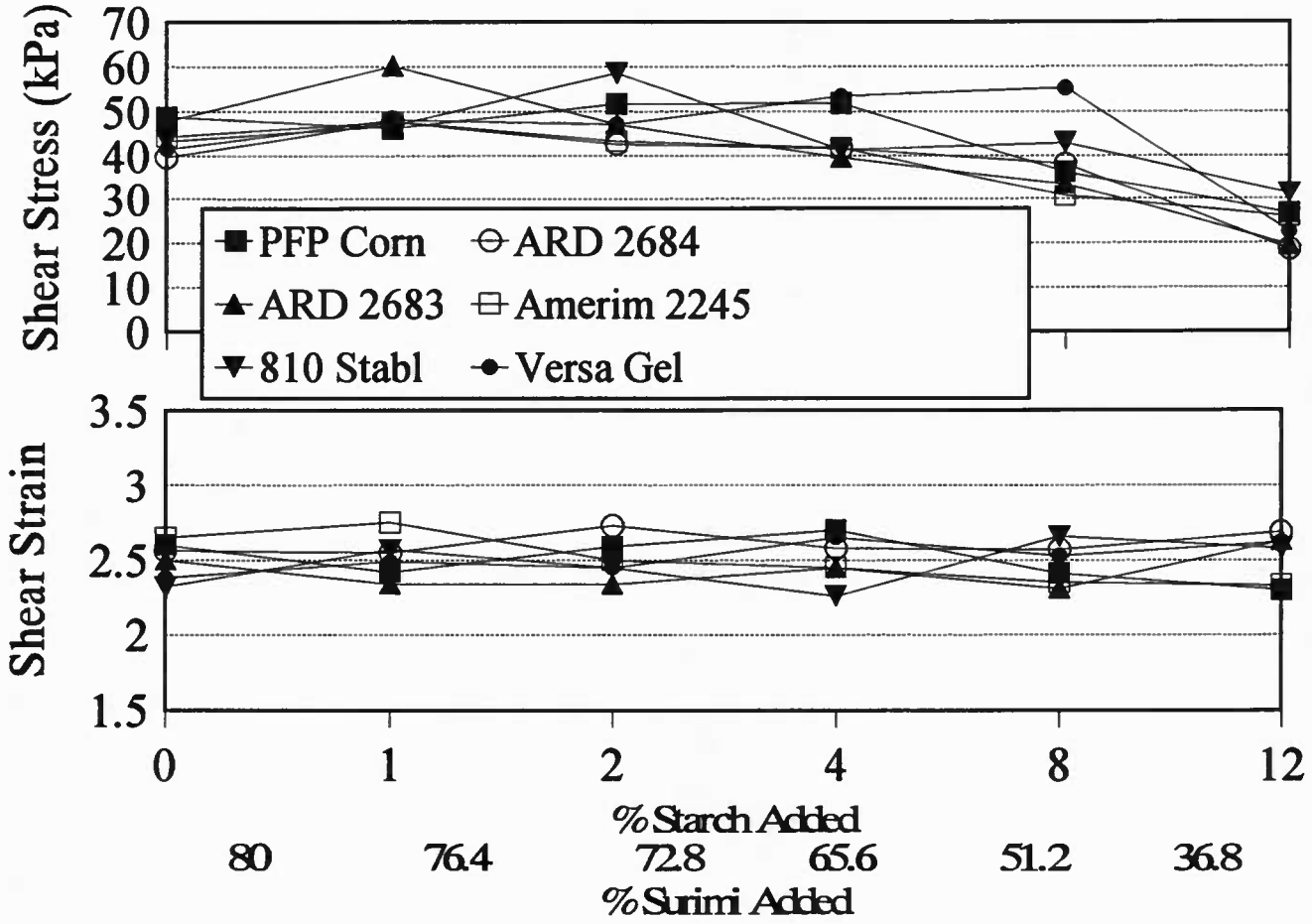

Figure. A.1 - Textural Strength Tested at 5°C (Cold Serving).

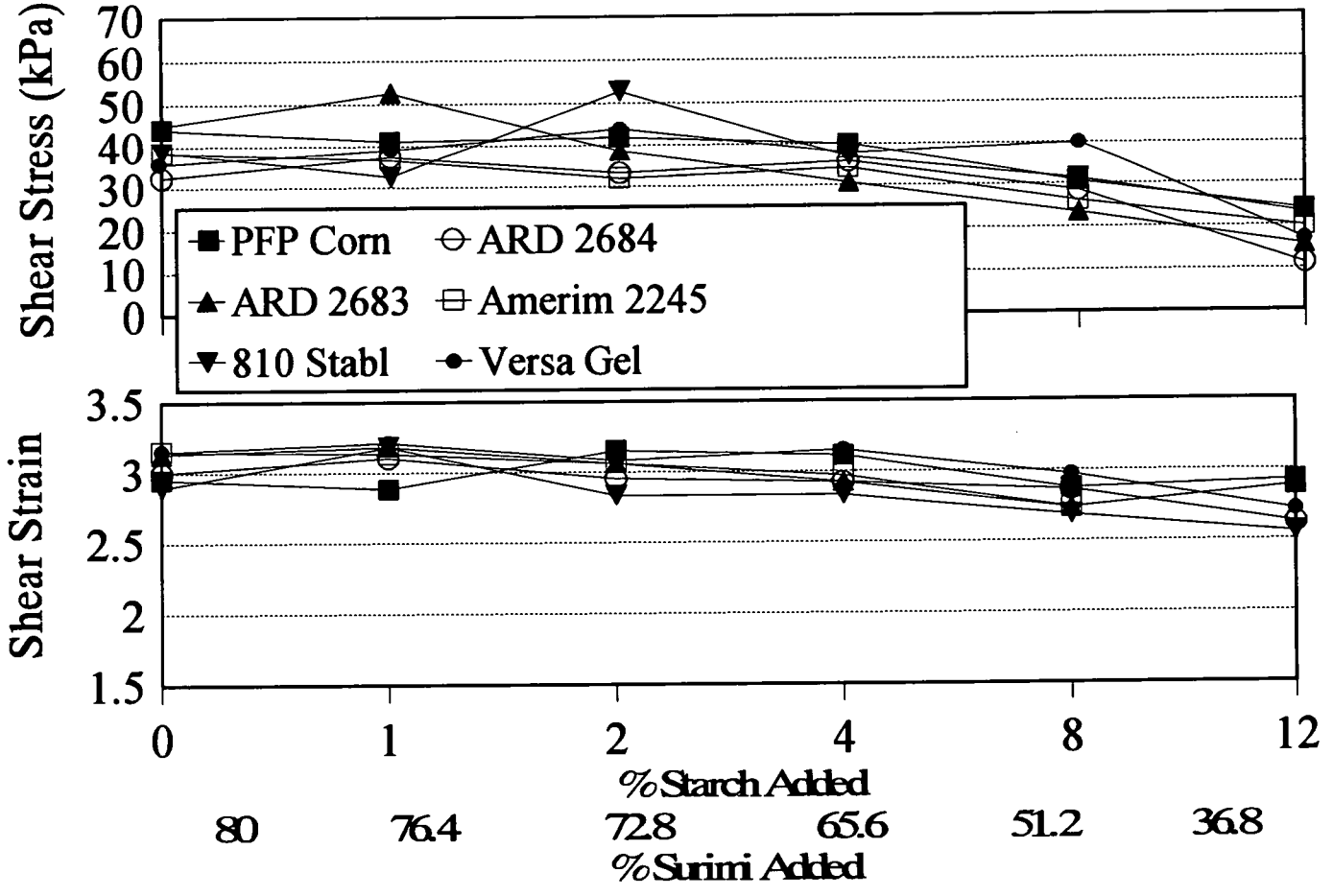

Figure. A.2 - Textural Strength Tested at 50°C (Warm Serving).

dependent on temperature. Hydrogen bonds, stabilizing alpha-helix and beta-sheet structure in cold gel, are enhanced at cool temperature; whereas, hydrophobic interactions increase at warmer temperatures maximizing at ~60°C (Niwa, 1992; Cheftel et al., 1985). Shear stress were dependent oppositely on the test temperature due to dependence of shear stress on the hydrogen bond (Howe et al., 1994). In a cold condition, fracture stress increased as hydrogen bonding was enhanced. In warmer conditions, although hydrophobic interaction increased, it could unlikely compensate for a decreased hydrogen bonding since the energy of hydrogen bonding (8-40 kJ/mol) was larger than that of hydrophobic interaction (4-12 kJ/mol). However, shear strain may be insensitive to hydrogen bonds but was strongly affected by hydrophobic interactions (Hamann and MacDonald, 1992). As the temperature of gels increased, the influence of hydrophobic interactions was enhanced and so was shear strain. The changes in shear stress and shear strain showed no difference between gels with and without starch when test temperature changed from 5° to 50°C (Fig. A.1 and A.2). There were no differences shown for all starches. Starch, with or without modification, did not affect property of gels of which shear stress and shear strain were changed based on change in test temperatures. The starch granule fills in the gel matrix and is not involved in the gel network structure (Okada, 1986). The swollen starch granules applied pressure to the gel matrix, however, they did not affect function of the protein. Hence, shear strain changed less with exception of the gel with the highest starch content (>8%).

Sensory characteristics of surimi gel texture in relation to shear stress and shear strain are categorized: *mushy*: low stress, low strain; *brittle*: high stress, low strain; *rubbery*: low stress, high strain; *tough*: high stress, high strain (Lanier, 1986). As temperature increased from 5° to 50°C, shear stress decreased and shear strain increased. Hence, the starch-surimi gel became more brittle at cold temperature and more rubbery at warm temperatures.

Shear stress changed with respect to the type and contents of starches at the same temperature (Fig. A.1 and A.2). Shear stress increased greatly in low starch content, except for Amerimaize 2245. When the starch content increased, shear stress decreased gradually. Shear stress was greatly affected by protein concentration, processing conditions, and ingredient variables (Lanier, 1986; Hamann, 1988). When starch was added at the highest content, shear stress decreased depending on the type of starch. This may occur when the protein matrix contains too many starch granules and maximum reinforcing influence of starch can not be obtained (Lee and Kim, 1986b). The gelatinization of starch granules, which is accompanied with the heating gelation of surimi proteins, allows the swollen granules to disperse in the matrix and result in increased rigidity (Wu et al., 1985b). When an additive forms the primary structural network by itself, the textural properties are more dependent on that gel network (Lanier, 1986). With a lower protein content, fracture stress decreased (Howe et al., 1994; W.B. Yoon and J.W. Park, unpublished data). Therefore, in lower starch contents, the strength of gels was enhanced; in higher starch content, although the starch increased the gel strength, the

properties of the "starch" gel resulted in decreased strength of the surimi-starch gel. Reduction of shear stress at the higher content of starch might have been due to a decreased surimi content and its competing starch granules for available water. However, although surimi concentrations were changed from 80% to 36.8%, the values of shear strain of all surimi-starch gels changed less (Fig. A.1 and A.2). Shear strain of modified starch-surimi gels was not affected by the addition of 5% starch (Wu et al., 1985b). Shear strain is a constant measure of protein functionality (Lanier, 1986; Hamann, 1988). However, a significant increase of shear strain values of pollock-starch gels was observed when 3% starch was added, except for modified waxy maize (MWM) starch (W.B. Yoon and J.W. Park, unpublished data). MWM showed its ability to increase the cohesive nature of gels as its content increased beyond 3%.

Effects of Freeze/Thaw on Expressible Moisture, Textural Properties, and Color.

Freeze/thaw abuse was repeated up to 9 cycles to simulate long term frozen storage. Expressible moisture indicated the amount of water wept from the gel structure of protein by applied force, and is oppositely proportional to water holding capacity (Jauregui et al., 1981). Fig. A.3 illustrated expressible moisture of surimi-starch gels as affected by freeze/thaw cycles. There was a significant difference between corn starch and modified starches; especially, when the starch contents were 2% or higher. In the gels with corn starch, expressible moisture markedly increased during freeze/thaw cycles. Expressible moisture of other gels with modified starches remained constant during the freeze/thaw storage. However, the higher the content of modified starch, the

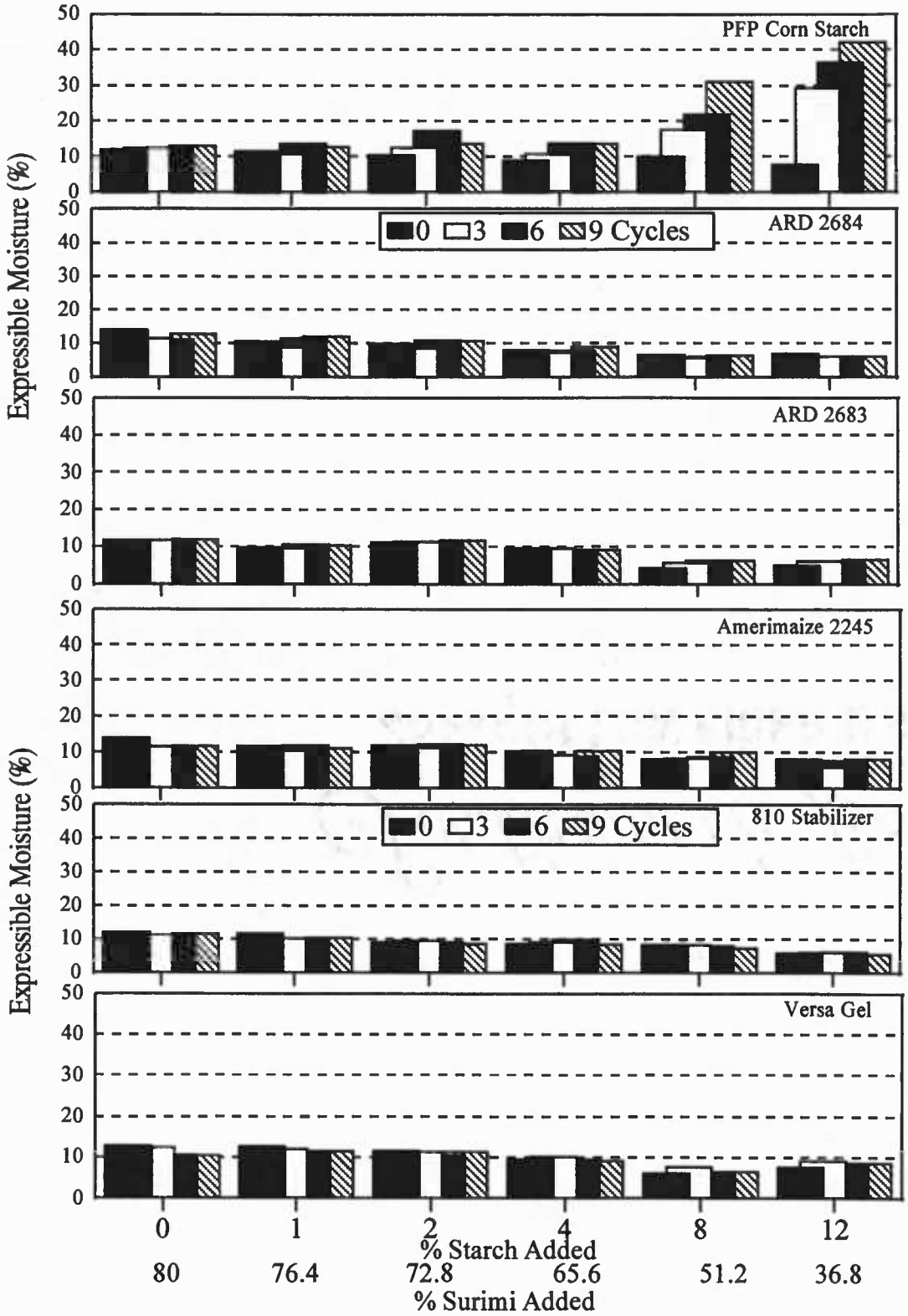

Figure A.3. Expressible moisture during freeze/thaw abuse.

lower the expressible moisture. Starches modified by hydroxypropylation or acetylation, with or without cross-linking, resisted retrogradation during freeze/thaw abuse (Lee et al., 1992). The hydroxypropylation and the acetylation decreased the gelatinizing temperature, reduced tendency to retrograde, was freeze/thaw stable, and possessed cold storage stability. Crosslinking makes the granules tough so that the integrity of the swollen granule is maintained on swelling, minimizing the release of amylose from the swollen granule (Tuschhoff, 1986; Jarowenko, 1986; Wurzburg, 1986a). Corn starch contains 25% linear amylose and 75% branched amylopectin. With its linearity, mobility, and hydroxyl groups, amylose has a tendency to become a parallel or crystalline style and draw closely enough to allow hydrogen bonding between hydroxyl groups on adjacent amylose (Wurzburg, 1986b). Expressible moisture of surimi-starch gel is sensitive to amylose due to its retrogradation (Kim and Lee, 1987). Linear amylose of gels was readily associated together (retrogradation) during the cooling temperature, so syneresis took place and resulted in a release of free water (Lee et al., 1992). This released free water deteriorates the textural properties of gels. However, with no amylose to retrograde, expressible moisture of modified waxy starch-gels remained less changeable since branched amylopectin does not fit together. There were larger-sized ice crystals and less concentrated ice crystal density in unmodified starch-surimi gels, and inversely in modified starch-surimi gels (Lee and Kim, 1986a). When surimi content was higher than 65.6%, the effects of freeze/thaw were not noticeable because protein contents were enough to maintain the textural integrity (Fig. A.3). Although 810 Stabilizer contained 25% linear amylose, it resisted retrogradation during freeze/thaw abuse because it was

hydroxypropylated and cross-linked. Based on these results, it is evident that modified starch plays a very important role in stabilizing surimi gels during freeze/thaw abuse. Without modification, native starch could not hold water during long periods of frozen storage.

In Fig A.4, it was shown that when the starch content was less than 4%, shear stress decreased during freeze/thaw cycles except Versa Gel; but when starch content was 8% or more, the strength of gels did not change or slightly increased, especially surimi gels with 8% Versa Gel. It seemed that the proteins, which formed the gel structure, were weakened during freeze/thaw abuse. Modified starch maintained or increased the strength of the network structure because it significantly minimized textural deterioration due to freeze/thaw. The capacity of maintaining and increasing the strength of the gel was in proportion to the contents of modified starches. However, heat-induced gelation of myofibrillar proteins mainly contributed to the network frame of gels (Lanier, 1986). Even though modified starch maintained or fortified the strength, the strength of gels began to decrease when the content of surimi protein decreased to a certain degree. Namely, the fortification of modified starch could not compensate for the decreased network structure due to the lower content of proteins. It also happened at different test temperatures when the starch contents were higher than 8% (Figs. A.1 and A.2). When 1% starch was added, 810 Stabilizer and Versa Gel performed the most effectively among all modified starches during freeze/thaw cycles. Versa Gel starch maintained the strength of gels during freeze/thaw and maximized at 8%. Functionality of gels with PFP

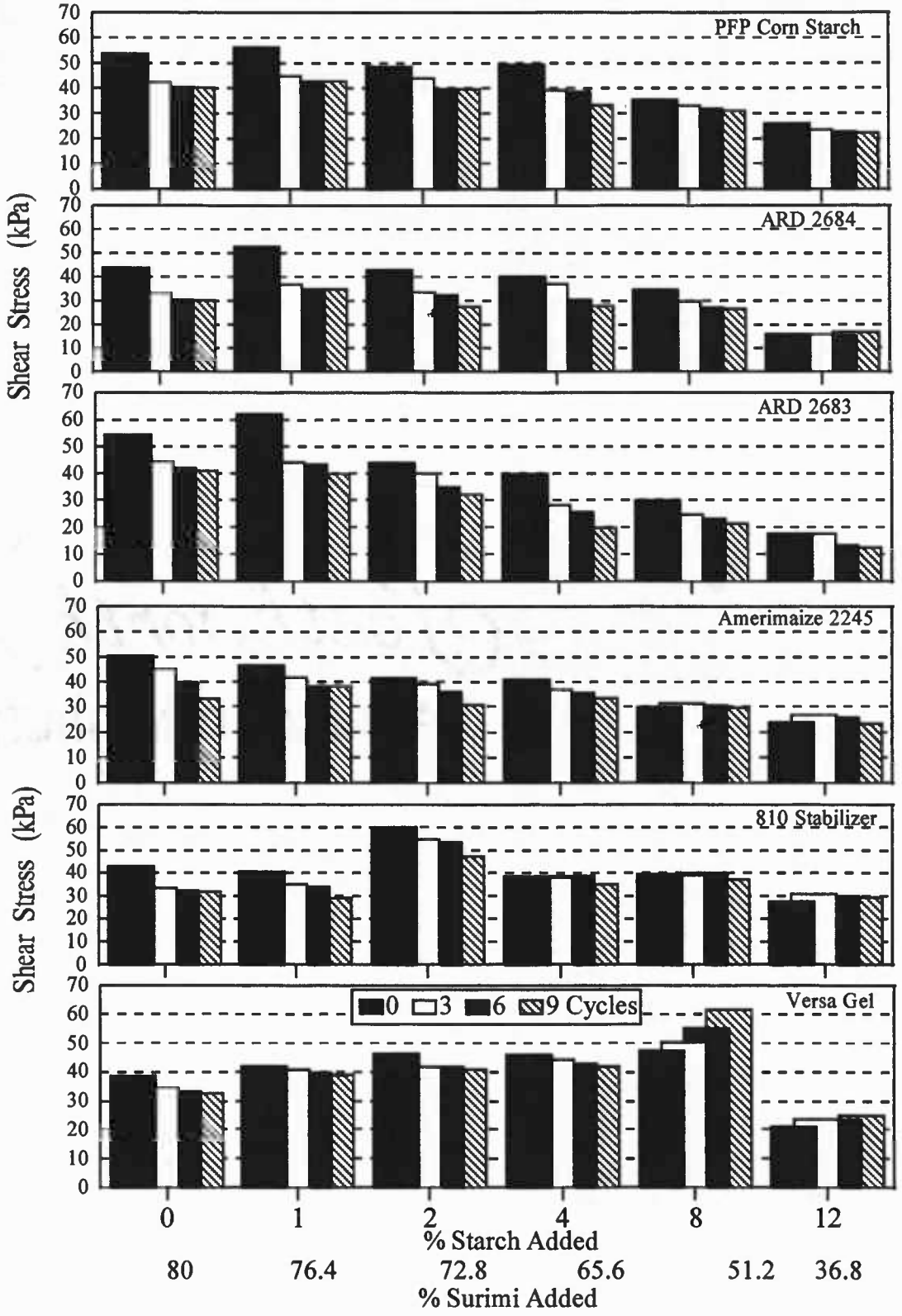

Figure A.4. Textural stability during freeze/thaw abuse.

decreased during freeze/thaw abuse. Retrograded amylose released free water (weeping) so that formation of bigger ice crystals might have deteriorated the textural structure resulting in decreased strength (Fig. A.4). Effect of freezing cycles was minimized as surimi content decreased (inversely, starch content increased). Shear strain changed less during freeze/thaw cycles, except 12% content of PFP, ARD 2683, and Amerimaize 2245 (not shown). Compared with expressible moisture, gels with 12% PFP corn starch content showed the highest value of expressible moisture after 12 cycles of freeze/thaw. It illustrated that the structure of protein gels was significantly affected by freeze/thaw abuse unless appropriate modified starch is used.

Gel color is very important for quality of surimi seafood products (Park, 1995b). L* value indicates lightness, while b* value denotes yellowness (+) and blueness (-). In Fig. A.5 and A.6, L* and b* values of unfrozen gels decreased continuously as starch content increased and gels gradually became more translucent except gels with PFP. This was probably due to the change of b* from "+" (yellow hue) to "-" (blue hue). During freeze/thaw cycles, L* and b* value decreased when the starch content was less than 8% and increased when the starch content was 8 and 12% except PFP corn starch. Freeze/thaw abuse greatly reduces lightness of surimi gels and slightly decreases yellowness (Park, 1995b). This probably indicated that the influence of adding starch decreased lightness and decreased yellow hue (inversely increased blue hue) during freeze/thaw. Effects of freeze/thaw on colors of gels were more pronounced in the case

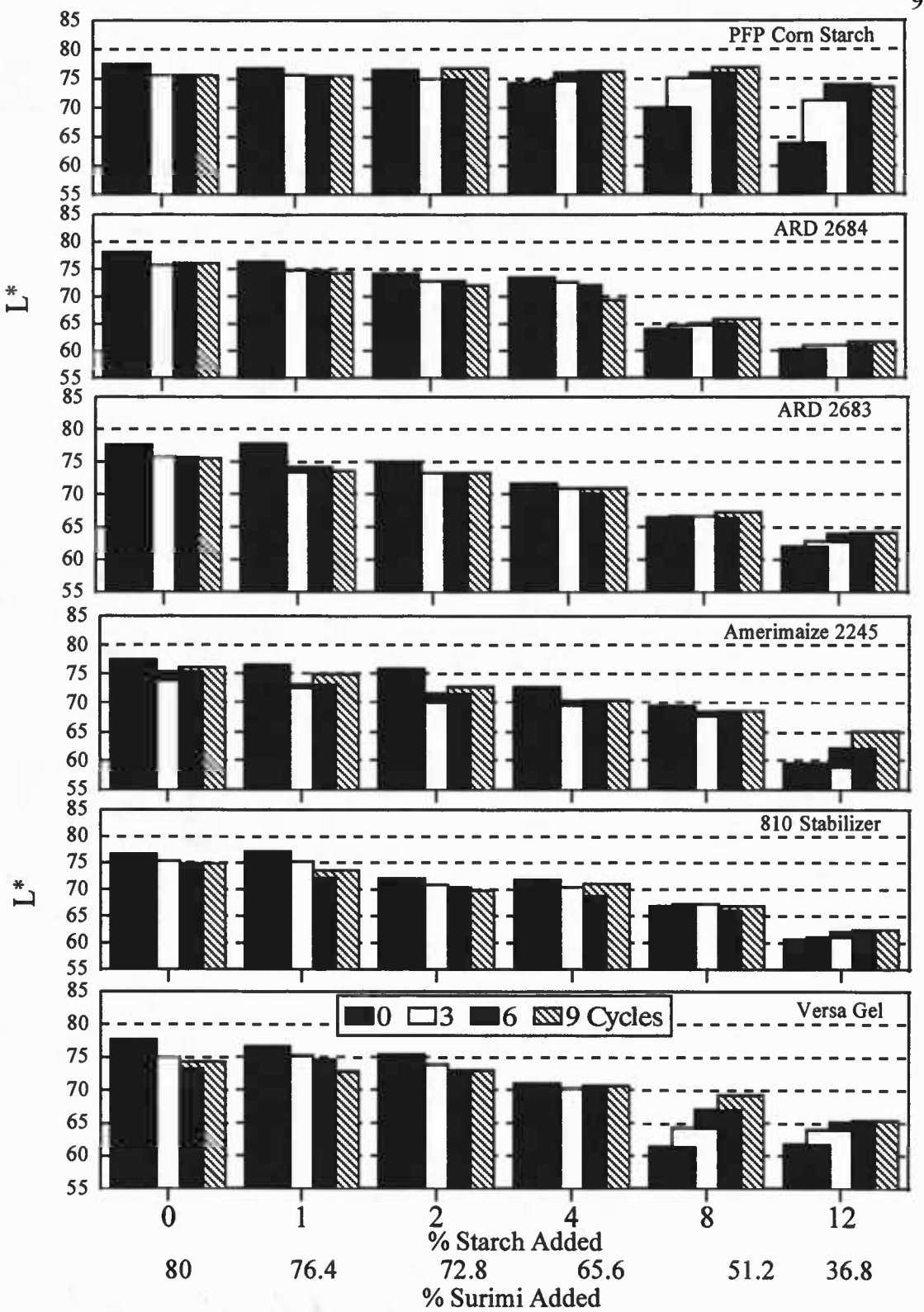

Figure A.5. Color (L*) value during freeze/thaw abuse.

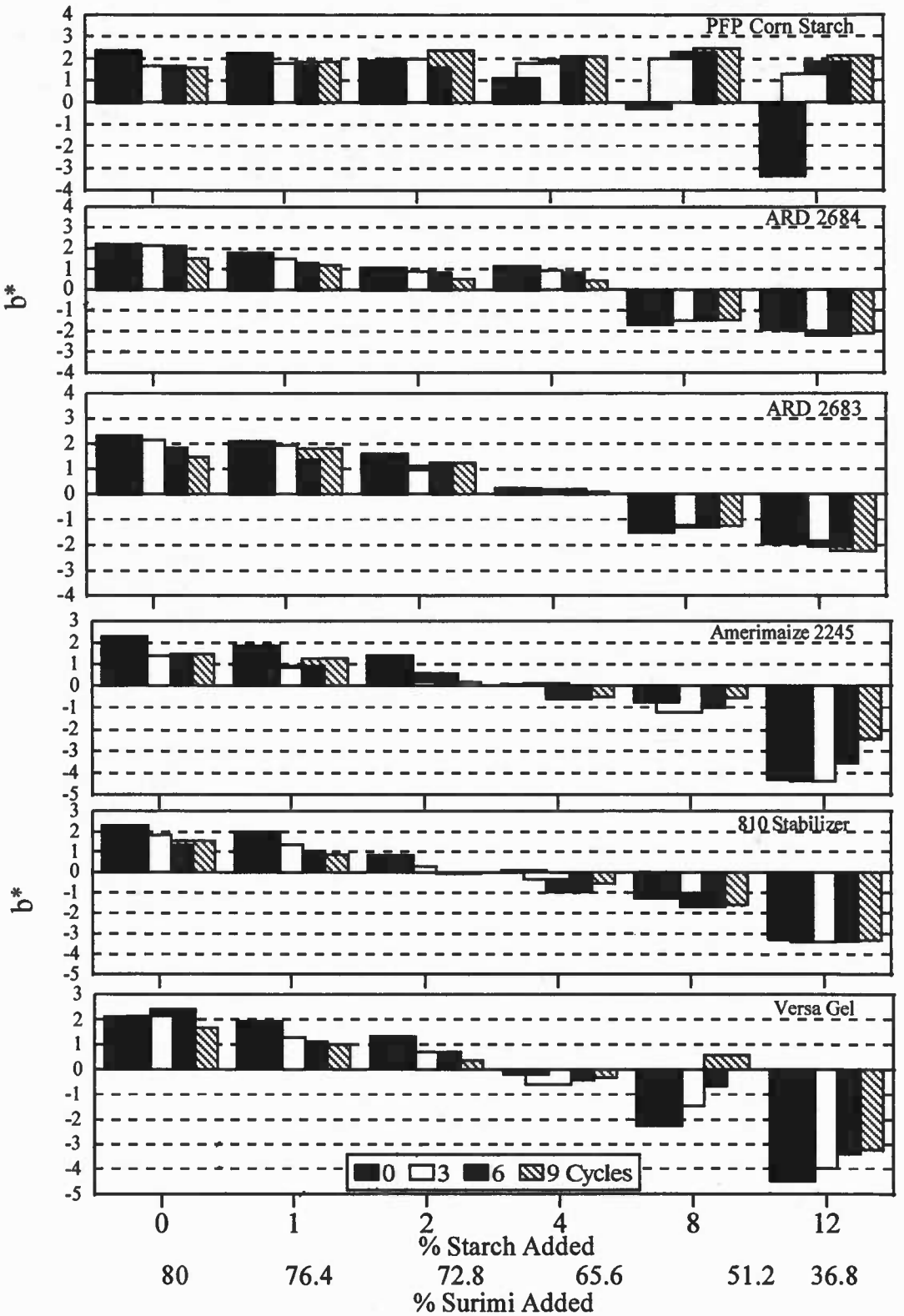

Figure A.6. Color (b*) value during freeze/thaw abuse.

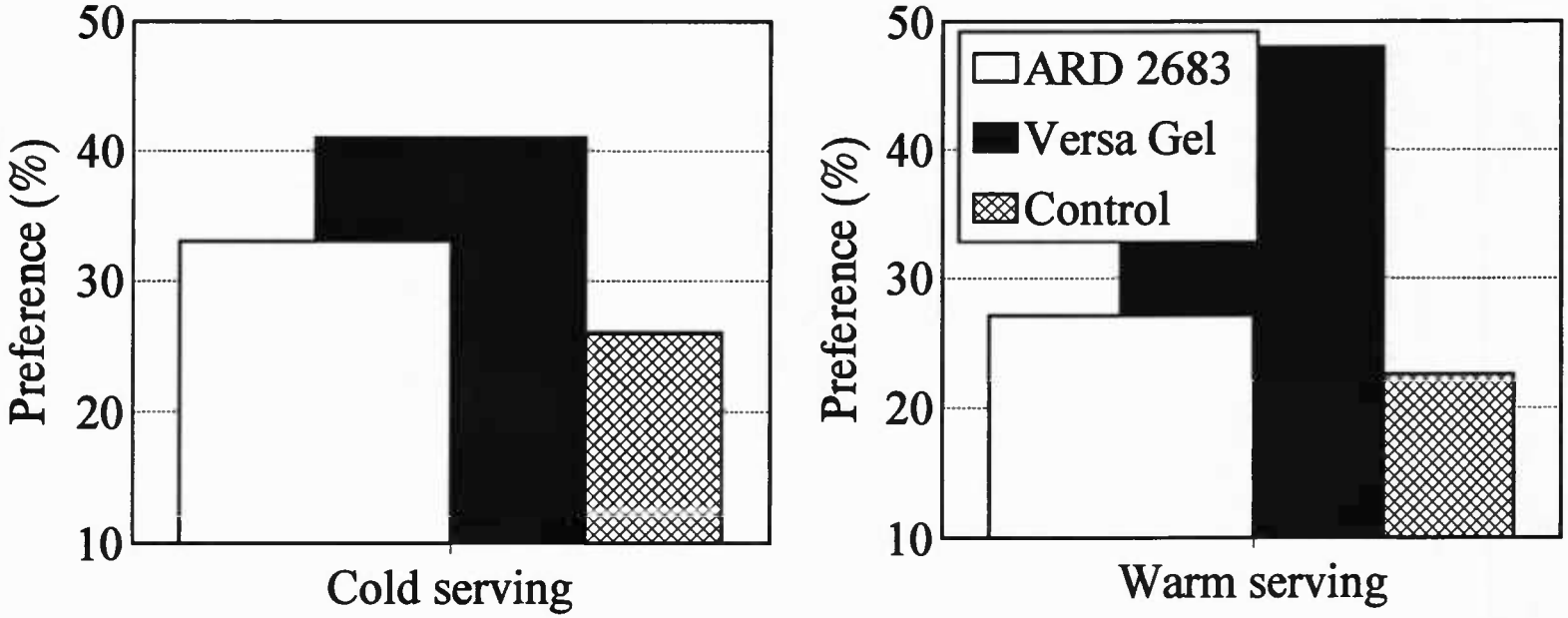

Figure. A.7 - Consumer's Preference on each serving.

of higher content (8, 12%) of PFP corn starch. Lightness increased and blueness (-b*) changed to yellowness (+b*) as the cycle of freeze/thaw increased.

Consumer Taste Panel

In cold servings of surimi-based crabmeat, 2% 810 Stabilizer was most preferred, while warm serving crabmeat, with 2% Versa Gel, were significantly preferred by consumers (Fig. A.7). Differences in springiness and hardness for both applications were detected by consumers. However, consumers did not detect a difference in mouth coating among samples served at both temperatures (not shown). This maybe due to consumer's unfamiliarity of the sensory terminology.

Conclusions

Shear stress of gels increased with the addition of lower content of starch into surimi and decreased at higher starch content depending on the nature and modification of starch. Reduction of shear stress at the higher content of starch might have been due to a decreased surimi content and its competing starch granules for available water. Shear strain was rather consistent or slightly increased at starch 4% or less. Gels, regardless of starch, became more brittle at cold temperatures and more rubbery at warm temperatures. During freeze/thaw cycles, shear stress and shear strain greatly decreased with PFP corn starch or lower modified starch contents, while they were well maintained at higher

modified starch contents. Expressible moisture of the gel also was significantly minimized with the increased contents of modified starches. L* and b* values of the gel color decreased with the addition of the starches. During freeze/thaw cycles, L* value decreased with low starch contents and increased with high starch contents. For the b* value, yellow hue (+) continued to decrease to become blue hue (-) as the starch content increased except for PFP corn starch. According to the consumer taste panel, 810 Stabilizer performed well in cold serving surimi-based crabmeat, while Versa Gel in warm servings.

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