

Review

Surimi – minced and washed fish meat – has primarily been produced from white-muscle fish species, since the desirable odor, light color and gel-forming characteristics of the resultant surimi are very important to enable further processing to heat-induced gel products such as crab leg analog. The production of lowfat surimi with desirable gel-forming characteristics from sardine and mackerel by conventional processing methods has had only limited success; however, recent developments have opened the way to the utilization of red-meat fish for surimi production. During surimi processing, the loss of water-soluble proteins into the wash water leads not only to the waste of certain valuable nutrients but also to pollution of the water; new methods for the recovery of water-soluble proteins from the wash water are described. The role of cryoprotectants in improving frozen surimi storage is explained by the glass transition concept.

Originally the term 'surimi' referred to minced and water-washed fish muscle tissues, while it has now also been accepted to refer to crab leg analogs, a surimi-based product, in Europe and in North America. In this review, 'surimi' will be used to refer to minced and water-washed fish muscle tissues; its frozen products will be denoted 'frozen surimi'.

Although Alaska pollock (*Theragra chalcogramma*) has been the most utilized raw material for surimi processing, its muscle tissues are not necessarily suitable for use in other fish products. They are too soft to handle during processing and are very susceptible to quality deterioration. Once the muscle tissue has been frozen and subsequently stored at a low temperature, the thawed muscles tend to be spongy¹ and, therefore, its value as merchandise is drastically reduced. These undesirable changes in the frozen muscle tissues are believed to be due to the formation of formaldehydes² and to the accumulation of peroxidized lipids³ in the muscle tissues during relatively long periods of frozen storage. Thus, up to the time when a nearly completed surimi technology was commercialized in the 1960s (Refs 4–6), there was little use of Alaska pollock muscle tissues as food and foodstuffs, except in the northern regions of Japan where these fish species are readily available.

Repeated washing of the minced muscle tissues with fresh water is the most characteristic and indispensable stage of surimi processing; this treatment is effective in removing certain factors that accelerate protein denaturation into the waste water and in improving the stability of the gel-forming characteristics of surimi during frozen storage. New developments in the use of

New developments in surimi technology

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cryoprotectants to protect the minced and washed fish muscle tissues against protein denaturation during subsequent frozen storage mean that surimi, developed primarily in Japan, is now produced and consumed as a foodstuff all over the world. The ready availability of Alaska pollock in the North Pacific may have contributed to the recent increase in the output of surimi⁷. Furthermore, the high level of quality nutrients in surimi and its products matches that of land-animal meats. Indeed, the overall amino acid score of surimi is that of a high-quality protein, and is similar to those of beef and turkey^{8,9} (Table 1).

Modern surimi processing

The overall process of modern surimi production is summarized in Fig. 1. Alaska pollock is caught by mid-water and bottom trawlers. The fish should be handled carefully since fish freshness affects the quality of the surimi; fresher fish results in higher-quality products. The body temperature of the fish should be kept just above the freezing point prior to processing, stored in crushed ice or in refrigerated sea water. In addition, the

Table 1. Chemical scores for essential amino acids in surimi, beef, pork, chicken and turkey^a

Essential amino acid	Pollock surimi	Beef	Pork	Chicken	Turkey
Histidine	147	171	300	182	182
Isoleucine	148	121	114	126	124
Leucine	151	120	116	107	114
Lysine	229	165	195	167	184
Methionine and Cystine	158	142	146	158	150
Phenylalanine and Tyrosine	101	99	104	101	110
Threonine	131	114	120	120	126
Tryptophan	118	100	109	109	100
Valine	102	119	104	104	110
(Overall score) ^b	(101)	(99)	(104)	(101)	(100)

^a Data taken from Ref. 9

^b The overall chemical score for a protein is that of the lowest score for a single amino acid (the limiting amino acid). For surimi, the aromatic amino acids are limiting

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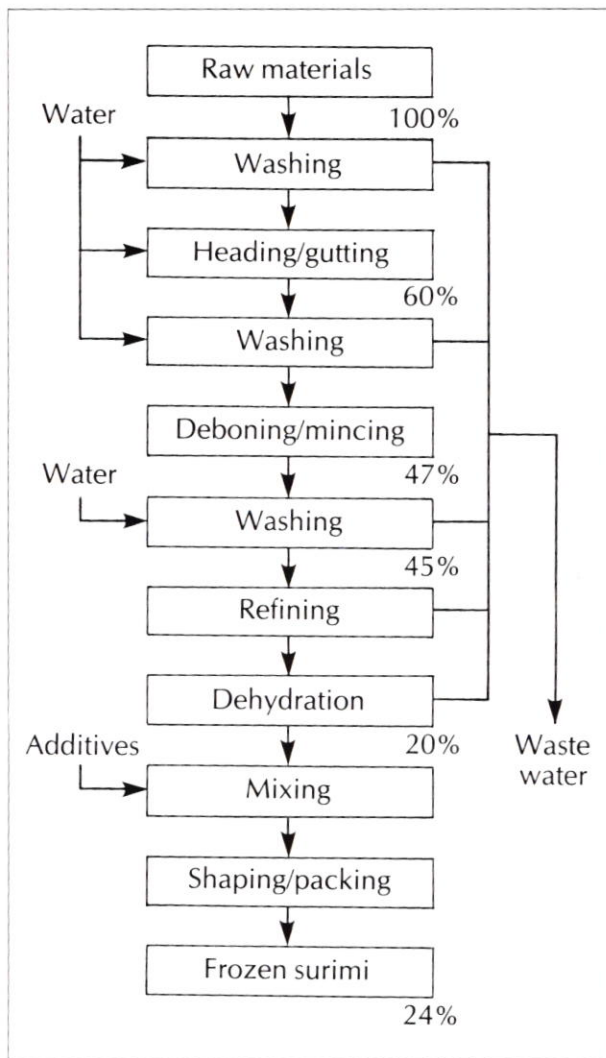


Fig. 1
Flow diagram of frozen surimi production.

fish should be delivered for subsequent processing within 130 hours of harvest in order to produce the highest-quality surimi. Washing the fish by dipping in refrigerated seawater for 60 hours prior to evisceration results in a high-quality product⁹.

Heading, gutting, deboning and mincing

The head, viscera and a major part of the backbone are removed with a header/gutter, followed by filleting with a mechanical filleter. Should any amount of viscera become mingled with the fillets at this stage, proteolysis by the enzymes found in the viscera will reduce the quality of the surimi¹⁰. The accumulation of high levels of fat from the viscera is also undesirable for producing high-quality surimi. Since fish oils are rich in polyunsaturated fatty acids, with up to six unsaturated bonds per molecule¹¹, surimi containing a high level of fat tends to undergo lipid oxidation. Therefore, degutting should be completed at this stage, although this reduces the recovery of fillets to some extent. Generally, the recovery of fillets after this stage of processing accounts for about 60% of the raw materials, on a wet-mass basis.

During subsequent processing, the muscle tissues are separated and removed from the skin tissues of the fish fillets using a mechanical deboner. The crude muscle tissues thus obtained are then extruded over a rotating stainless steel drum with small pores to obtain the minced meat. The recovery after this stage accounts for ~47% of the raw materials.

Washing

The next stage of processing is very important since it has a direct influence on surimi quality. Usually, three or four separate tanks each filled with cold fresh water are used in washing the minced meat. Most sarcoplasmic proteins, including digestive enzymes such as proteases, lipases and phospholipases; inorganic salts; and water-soluble compounds such as trimethylamine oxide, formaldehydes and blood are removed by the washing process. The total protein contents show seasonal variations even within the same fish species; however, the contents of sarcoplasmic proteins and myofibrillar proteins are relatively stable, accounting for 18–20% and 65–80% of the total protein, respectively. The myofibrillar proteins, consisting of actin, myosin and tropomyosin, are insoluble in water but are easily extracted using up to a 0.6M salt solution. The ideal duration of washing depends on the properties of the minced meat, the water temperature, and chemical characteristics such as the pH and the ionic strength of the washing water. Gentle stirring for 9–12 minutes with 3–4 repeated washings in separate tanks each filled with fresh water are commonly used¹².

High concentrations of Ca^{2+} and Mg^{2+} in the wash water not only decrease the temperature tolerance of the minced meats during the washing process¹³, but also accelerate the denaturation of actomyosin in the frozen surimi during storage¹⁴. Thus, the acceptable range of ionic strengths of the wash water is believed to be 0.005–0.1. The pH of the wash water is related to the water-holding capacity of the fish muscle proteins and, hence, the gel-forming characteristics of the final product¹⁵, and thus affects the suitable volume of wash water¹⁶. Usually, the pH of the wash water is adjusted to that at which the fish muscle should be processed.

It is well accepted that the heat stability of myofibrillar proteins of fish muscle adapts itself to the temperature of the waters normally inhabited by the fish¹⁷. Studies of the Ca^{2+} -ATPase activity (used as an index of heat-setting ability) of several fish actomyosins¹⁸ have shown that the actomyosin of cold-water fish species denatures at lower temperatures¹⁹. In general, fish myofibrillar proteins are much more susceptible to heating than, for example, rabbit myofibrillar proteins¹⁹. The temperature tolerance of Alaska pollock is ~10°C, so the temperature of the wash water should theoretically be below 10°C in order to prevent protein denaturation. However, the extraction of undesired sarcoplasmic proteins from the minced fish meats into the wash water increases with increasing water temperature²⁰; thus, additional washing steps are necessary when lower wash water temperatures are used. Therefore, the

temperature of the wash water is decided upon after balancing these opposing factors.

The recovery of the minced and washed meats after the washing stage accounts for ~45% of the raw materials. Although this is apparently higher than the recovery from the previous stage, this is merely due to an increase in the wet mass due to water being held in the protein residues.

Refining and dehydration

The washed meats are passed through a refiner to remove any remaining small bones, skin tissues, dark muscle tissues and scales. The refiner is a high-speed rotary spiral surrounded by a screen with many small pores 1.2–3.2 mm in diameter. It is important to operate the refiner at a low temperature in order to prevent protein denaturation. Excess water being held in the washed meats is then removed using a screw press; the moisture content is reduced from 90% in the refined meats to 80–84% in the dehydrated meats. The moisture level after the dehydration process depends on the washing steps: the temperature, pH and ionic strength of the washing water, the mixing ratio of meat and washing water, etc. If the water-holding capacity of the washed meats is too high to permit satisfactory dehydration, 0.2% NaCl is usually added to the washing water to decrease the water-holding capacity of the washed meat. The recovery of well-dehydrated minced and washed meat is ~20% of the raw materials.

Use of additives

The amount of cryoprotectants added to the dehydrated meats depends on the intended storage period of the surimi. In general, 4% sucrose or 4–5% sorbitol is added to the dehydrated meats in addition to 0.2–0.3% polyphosphate. Although polyphosphate alone does not appear to be an efficient cryoprotectant, polyphosphate together with sucrose or sorbitol is more effective than sucrose or sorbitol alone. Added sucrose is sometimes undesirable as it imparts a sweet taste to the surimi and causes browning during frozen storage²¹; therefore, polydextrose is usually used instead to avoid browning²². The surimi with added cryoprotectants is packed in a freezing pan and frozen quickly to below –25°C using a contact freezer. The recovery of the final products accounts for 24% of the raw materials. Frozen surimi is then stored in a freezer controlled at –25°C or lower.

Gelation of the washed mince occurs as a result of heat-induced dissociation of the actin–myosin (actomyosin) complex followed by the formation of covalent bonds between myosin chains. In order to produce surimi-based gelled products such as kamaboko, relatively high concentrations of salt (up to 3%) are added to the surimi to induce dissociation of the actomyosin, allowing the subsequent sol–gel transition to occur at room temperature. The gel is then stabilized by heating to induce the formation of limited amounts of actomyosin, which acts as a crosslinker between the ‘tails’ of the bound and free myosin molecules²³.

Glass transition during the freezing of surimi

Sucrose and polyphosphate are used empirically as the primary cryoprotectants in surimi processing. However, most mono- and disaccharides, low molecular weight polyols²⁴, and certain amino acids²⁵ and nucleotides²⁶ are also known to have cryoprotective effects. There have been some efforts to understand the mechanism of cryoprotection and to search for novel cryoprotectants, including polymers such as dextran and polyethylene glycol.

The mechanism of cryoprotection by both low molecular weight carbohydrates and polymers may be understood in terms of the glass transition concept, even though low molecular weight carbohydrates stabilize proteins thermodynamically through their interaction with the surrounding water. The concept of the glass transition was introduced to the field of food science relatively recently²⁷. Glass transition behavior is particularly relevant to the freezing of foods. A ‘glass’ is an amorphous solid that has a liquid-like structure with a viscosity greater than 10¹⁴ Pa·s (Ref. 28). As the temperature falls, the liquid viscosity increases and the translation movement of the molecules becomes slower. When molecular translation cannot occur within the experimental timescale, the variation of enthalpy and volume with temperature will resemble those of a solid, even though the molecules are not ordered, as in a crystalline structure. The transition point from liquid-like to solid-like behavior denotes the glass transition temperature, T_g .

It is known that many sugars and polymers will form glasses. As shown in Fig. 2, the T_g of binary systems such as sucrose solutions depends on the water content and on the physical and chemical characteristics of the solute. During practical freezing, an aqueous solution is gradually freeze-concentrated during the crystallization of pure ice. This process increases the residual solution viscosity so that the precipitation of solute cannot occur even if the temperature of the solution reaches that corresponding to the eutectic point (T_e). On further cooling a stage is reached at which ice crystallization practically ceases, at least on a realistic timescale: the glass transition. The residual, unfrozen glassy mixture is characterized by its glass transition temperature, T_g' , and by W_g' , its water content²⁹. Proteins and reactive species trapped in the glassy matrix below T_g' are very stable owing to the extremely high viscosity of the glass; several enzymes have been stabilized by freeze drying or spray drying to ‘trap’ the enzymes in a sugar solution kept below its glass transition temperature³⁰.

Although there have been extensive investigations into the freezing behavior of aqueous low molecular weight carbohydrate systems^{27,29}, the behavior of polysaccharide systems and protein systems has only recently been investigated. Upon freezing a protein–buffer solution with added sugar, if the initial protein concentration is low, the behavior of the system will be similar to that of a ternary sugar–buffer–water system. However, the state diagram of even a simple ternary system has yet to be determined. It has been reported

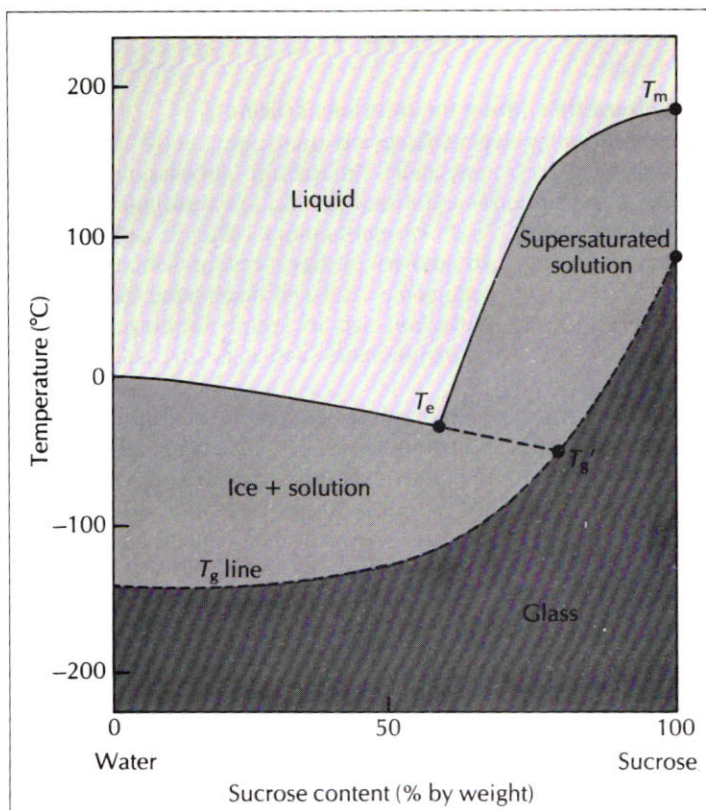


Fig. 2

Typical solid-liquid state diagram of the sucrose-water binary system. Solid lines correspond to solid-liquid equilibrium curves; the broken line from the eutectic point (T_e) to the glass transition point (T_g') indicates the actual pathway of the freezing process, and the broken line (T_g line) represents the change in the glass transition temperature (the point at which the viscosity of the solution is 10^{14} Pa·s) depending on the water content. Below this line, the homogeneous phase is a glass. T_m is the melting point of sucrose.

See text for more details.

that salts may precipitate from a buffer solution depending on its composition³⁰. In the case of solutions with high concentrations of protein, such as surimi, the situation is even more complicated.

Attempts have been made to explain the cryoprotective effect of sucrose or maltodextrin on surimi on the basis of the concept of the glass transition, using actomyosin as a model system³¹. The responses of the stability of actomyosin-cryoprotectant-water systems to storage temperatures were not consistently related to the glass transition temperatures of the corresponding cryoprotectant-water binary solutions. There is a need for further investigation of the glass transition behavior of more complicated systems such as solutions containing high concentrations of actomyosin or buffers.

During the freezing of surimi, as freeze concentration progresses the pH and salt concentrations change dramatically before the residual solution reaches its T_g' . The cryoprotectant sucrose is added to make the glass transition of the surimi system easier, and thus limit the freeze concentration effects. Polyphosphates, which are often added to surimi, are plasticizers and promote the dissociation of actomyosin; they may also play an important role in pH control³², but it is not clear why they are more effective than mono- and diphosphates.

One possible answer may lie in the different precipitation behaviors of the phosphates during freeze concentration. Preparation of the state diagram of the multi-component system including phosphates and sucrose will be necessary in order to understand the cryoprotection mechanism that occurs in surimi.

Waste water treatment

Although washing of the minced fish muscle tissues is an indispensable stage of surimi production, the washing process is itself linked with significant problems. The loss of sarcoplasmic proteins into the wash water not only leads to the wastage of some valuable nutrients but also sometimes causes pollution of the water by increasing its biological oxygen demand (BOD) and chemical oxygen demand (COD). A recent investigation showed that the COD values of the untreated waste water coming from surimi factors using 500–1000 t of wash water per day were 3000–4000 ppm (Ref. 33). These COD values have now been decreased by the application of pressure flotation and activated sludge methods³³. However, almost 30–60% of Alaska pollock muscle proteins, 34% of sardine muscle proteins and 39% of mackerel muscle proteins are lost during the washing process^{34,35}. For flying fish muscle tissues, the level of vitamin E decreased from 600 $\mu\text{g}/100$ g in the raw minced muscle tissues to 200 $\mu\text{g}/100$ g after three repeated washings, and the level of taurine in the free amino acids fraction decreased from 200 mg/100 g to 7.4 mg/100 g (Ref. 36). At least 5000 t (on a dry-mass basis) of sarcoplasmic proteins are estimated to have been lost to wash water during washing of the ~200 000 t of surimi that were produced in Japan in 1990 (Ref. 33). If certain functional components of fish muscle, such as the sarcoplasmic proteins, pigments, fats and oils can be recovered from the untreated waste water, then it will be possible to recycle the wash water as well as to utilize components that are presently wasted. There has been much research on methods to purify the waste water and to recover certain functional components.

'pH shifting'

A 'pH shifting' method based on the aggregation phenomenon of sarcoplasmic proteins has been applied to the collection of sarcoplasmic proteins from the waste wash water^{37,38}. The pH of the waste water is changed from 7 to below 4 and subsequently readjusted to 7–9 to obtain the proteins as precipitates. The recovery of proteins from waste water used in the processing of red-meat fish and white-meat fish is 90% and 70%, respectively.

Ultrafiltration

Ultrafiltration membrane systems using cellulose acetate have been used to reduce the volume of the waste water by passage through a tubular cellulose acetate membrane at a pressure of 0.49 MPa and a flow rate of 1.8 l/min (Ref. 39); 90% of the proteins in the waste water from red-meat fish are recovered using this

method. Many similar systems using different types of filter materials have been applied^{40,41}.

Coagulation

Most sarcoplasmic proteins in the waste water can be dissolved in NaOH at pH 10, followed by centrifugation to remove undissolved proteins. The pH is then adjusted to 5 by the addition of HCl, and the effluent is heated at 80°C to coagulate the sarcoplasmic proteins. The yield of recovered proteins is 20% of the protein content of the surimi products⁴².

New fish sources for surimi production

Japanese coastal red-meat fish

The lipid contents of red-meat fish such as sardine (*Sardinops caerulea*) and Pacific mackerel (*Scomber japonicus*) reveal seasonal variations, and reach ~10% of the muscle mass at most⁴³. Deterioration in the freshness of red-meat fish after rigor is usually rapid and the meat color is dark, since both the lipids and heme compound contents of dark muscle tissues are much higher than those of ordinary muscles⁴⁴. These characteristics make red fish meat unsuitable as a raw material for surimi production. More attention should be directed at developing methods to separate ordinary muscle tissues from the red muscle tissues. The dark meat is located just inside the dorsal lines⁴⁵, and therefore it is relatively easy to avoid contamination with red muscle tissues by removing a thicker portion of skin tissue. A jet stream of pressurized water has been successfully used to remove dorsal meat tissues from the skin tissues⁴⁶; however, this technique requires a large amount of fresh water.

Recently, a new technology has been developed to produce high-quality surimi with a low lipid content (~1.2%) and desirable flavor and color from red-meat fish. The surimi has satisfactory gel-forming characteristics upon heating. A feature of the technique is grinding of the ordinary meat tissues into 10–300 µm myofibrils⁴⁷; 4–8 volumes of cold 0.1–0.2% sodium pyrophosphate and 0.3–0.5% sodium bicarbonate in refrigerated 0.1% sodium chloride solution are added to one volume of ordinary muscle tissues and the mixture is ground *in vacuo* (10 mm Hg, 2400 rpm) for 30 minutes. Sodium bicarbonate is added to prevent denaturation of the myofibril proteins caused by a decrease in pH during the mincing. Sodium pyrophosphate enables the dissociation of actomyosin to form myosin and actin, improving the gel-forming characteristics of the surimi⁴⁸. Mincing *in vacuo* prevents drastic denaturation of the proteins and seems to accelerate the extraction of lipids and heme compounds into the wash water. The lipid contents of surimi thus produced from sardine and Pacific mackerel are 1.4% and 2.3%, respectively, lower than those of surimi produced using a conventional washing process⁴⁹. A slight fish odor is recognized organoleptically when the surimi is heated in hot water at 90°C (Ref. 49); the total quantity of volatile compounds formed on heating sardine surimi prepared by the novel method was half that formed by surimi

produced using a conventional method. Furthermore, the gel strength at 50°C of the novel surimi was greater than that of heated surimi produced by a traditional method. However, using red-meat fish species as the raw material for surimi production remains problematic, since the lipid contents of the muscle tissues show a wide variation from season to season. It is necessary to ensure that caught fish are processed without delay; the maximum storage duration in iced water until subsequent processing is just one day for sardine and two days for Pacific mackerel to ensure a high-quality product⁵⁰. Some characteristics of pollock surimi and sardine surimi, produced using the conventional method or the novel method, are compared in Fig. 3.

Southeast Asian tropical fish

The Marine Fisheries Research Department of the Southeast Asian Fisheries Development Center has developed a modern method for producing surimi from low-priced fish⁵². These fish species include coral fish (*Caesio* spp.), dorab (*Chirocentrus dorab*), bigeye snapper (*Priacanthus* spp.), threadfin beam (*Nemipterus* spp.), lizardfish (*Saurida* spp.), glassfish (*Pentaprion*

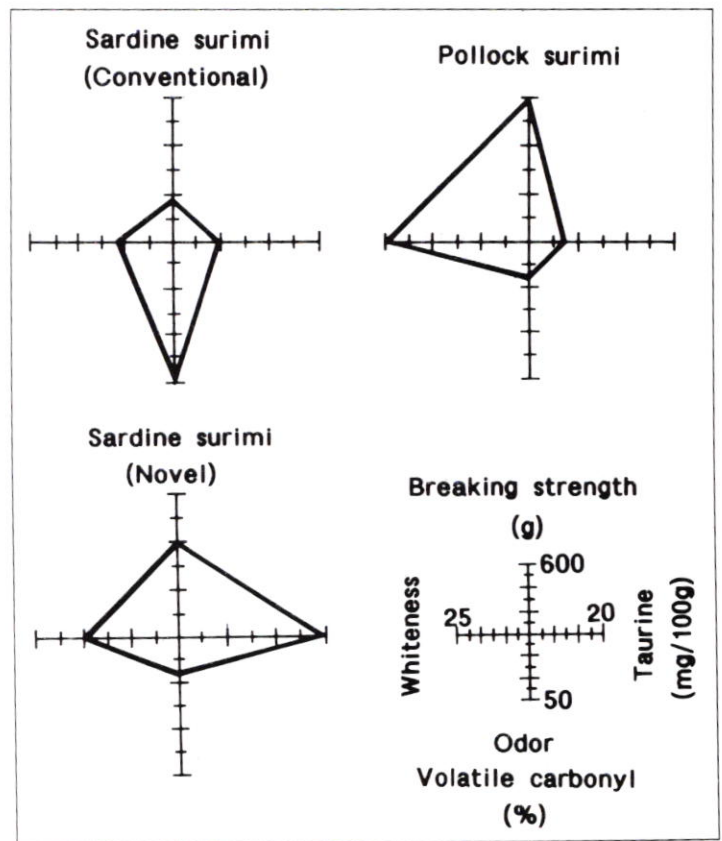


Fig. 3

Some characteristics of pollock surimi and of two kinds of sardine surimi produced by a conventional method and by a novel procedure. The taurine contents reflect the residual levels of water-soluble compounds in the surimis. Sardine surimi produced by the novel procedure is expected to contain more water-soluble compounds than conventional surimis. Data taken from Refs 47 and 51.

longimanus), small snapper (*Litjanus* spp.) and croaker (*Pennahia* spp.), which are trawled in the Southeast Pacific and Indian Oceans. The overall process of surimi production from these fish is very similar to that for Alaska pollock. One problem is that the muscle tissues of tropical fish tend to set irreversibly during processing, since the temperature is high in the areas inhabited by these species; thus, it is necessary to refrigerate the raw materials and the wash water. In 1989, 20 000–25 000 t of surimi were produced in Thailand. The majority is exported to Japan, but the amount of surimi exported from Southeast Asia to Europe as crab leg analogs is gradually increasing⁵³.

New Zealand white-meat fish

The lipid content of the muscle of hoki (*Macruronus novaezelandiae*) accounts for 1.6–3.7% of the mass. Although the period until the muscle tissues set is relatively short, this fish can be used as a raw material for surimi. The estimated biomass of hoki within the 200-mile fisheries conservation zone of New Zealand is 1.25×10^6 t; 0.25×10^6 t are allowed as an annual catch. The overall surimi production process is similar to that for Alaska pollock. Southern blue whiting (*Micro-mesistius australis*) is another promising raw material for the surimi industry. Its body is longer than Northern Atlantic whiting, and thus recovery of the final products as surimi is much higher. The chemical components of blue whiting are similar to those of hoki; proteins and lipids account for 18.9% and 0.8% of the mass respectively⁵⁴. The estimated biomass of Southern blue whiting is still uncertain; the annual catch is restricted to 60 000 t.

US West Coast Pacific hake

The annual catch of Pacific hake (*Merluccius productus*) on the West Coast of North America, from British Columbia to California, amounts to 175 000 t. The muscle tissues of Pacific hake have been regarded as low-grade food and foodstuffs, since the tissues become soft upon heating⁵⁵. This undesirable softening of the muscle tissues, caused by gelation, has been recognized not only in Pacific whiting but also in other fish species^{56,57}. Hence, the muscle tissues of Pacific hake have not traditionally been used for surimi processing, although its estimated biomass is very large. It has now been shown that certain proteases released by myxosporidia (*Chloromyxum musculiquefacience*; a parasitic protozoan that attacks fish) may induce the occurrence of heat-generated gelation of Pacific hake⁵⁸. Sodium dodecylsulfate polyacrylamide gel electrophoresis (SDS-PAGE) studies have shown that the proteases destroy the myosin heavy chains, which may explain the gel-forming ability of the surimi produced from Pacific hake⁵⁹. The effects of some protease inhibitors have been examined. The addition of 3% egg white to the muscle tissues decreases protease activity by 84% (Ref. 60); this technique now permits the practical use of Pacific hake for the surimi industries.

The future

It has traditionally been believed that only very fresh raw fish processed just after catching can be used to produce surimi of high quality. However, since catches are variable from season to season, it is important to develop new technologies to make it possible to use frozen fish as a raw material for surimi production. For red-meat fish such as sardine and mackerel, a drastic decrease in muscle pH *post mortem* leads to protein denaturation. Therefore, rapid freezing and low-temperature storage will be necessary to allow the utilization of this sort of fish.

As many countries have established their own technologies for surimi processing, it is necessary to develop an internationally recognized minimum standard that guarantees the quality of frozen surimi in order to maintain good trade relations between surimi-producing countries. The Codex Alimentarius Commission of the Food and Agriculture Organization has agreed to recommend that a code of practice for surimi should be elaborated⁶⁰ to ensure the high quality of surimi produced worldwide.

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