A Review of Surimi Production and Protein Gel Formation

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ABSTRACT

Surimi is meat that has been ground or minced and repeatedly cleansed and rinsed to remove the majority of the blood, odor, pigment, and fat. The traditional use of surimi, which was first created in Japan many centuries ago, as a raw ingredient for the production of kamaboko and other goods with a surimi base, is widespread today. Fish contain three main protein groups: sarcoplasm, connective tissue, and myofibrils, which are crucial for the production of goods based on surimi gel. Myofibril proteins, particularly myosin and actomyosin, must be dissolved in a high concentration of salt (NaCl), according to the hypothesis of gelling from fish muscle proteins that have undergone mincing and washing. Due to denaturation, interaction, and aggregation, this protein can gel when heated. A number of variables, including the type of fish, level of freshness, fishing technique, fishing season, growth stage, and fish size, will affect the ability to produce surimi of high quality. The handling of surimi raw materials must then be done correctly, from the ship to the location where the fish is processed. Everything must be done in a cold chain with consistent environmental sanitization and hygiene. This study seeks to give a general overview of how to create surimi in accordance with the references and information on the method for creating the distinctive gel of surimi, which is a crucial step in the creation of surimi-based products.

Keyword: *fish, gel formation, ingredient, protein, surimi*

1. INTRODUCTION

Surimi has important functional properties, namely the ability to form a gel and its ability to hold water (water holding capacity). Surimi can be produced from raw seawater fish or freshwater fish. Tilapia has been used as raw material for surimi production because of its availability and ability to form appropriate gels. It was reported that in 2000 the world's tilapia yields were around 1,266, 000 tons and that China produced 55% of the total world tilapia yields in 2002 [1].

Surimi is mashed or minced meat that is cleaned and washed repeatedly, therefore most of the blood, odor, pigment and fat are lost. Surimi was first developed in Japan traditionally since several hundred years ago and is usually used as a raw material for making surimi-based products, namely kamaboko. Surimi and its derivative products began to be popular in America in the early 1980s, at which time there was a shortage of King Crab and then a crab-like product developed but made with the basic ingredient of surimi called kanikama [2].

The various surimi-based products available today are based on Japanese processing technology and are the result of two breakthrough discoveries, namely the discovery of the use of cryoprotectants in surimi processing in 1960 and the discovery of artificial crab meat products derived from surimi [3]. To make good quality surimi, knowledge of fresh fish raw materials, protein properties, the effect of washing, addition of salt, addition of additives such as cryoprotectants and the effect of storage on the product is required hence that final processed products can be produced that are in accordance with the wishes and can still be accepted by consumers if we want

to sell it. This review aims to provide an overview of how to produce surimi according to the reference and provide information regarding the process of forming the characteristic gel of surimi which is an important key feature in producing surimi-based products.

2. FISH PROTEIN

2.1 Sarcoplasmic Proteins

These proteins are also called myogens and are mostly globular in shape. Included in this group of proteins are albumin protein, myoalbumin, myoprotein. These proteins are easily soluble in water. The amount of protein is not much, about 20 – 25% of the protein content of fish [4],[5].

Most myogens are enzymes that play a role in the formation of the odor and color of fish meat. Sarcoplasmic proteins also play a role in the process of glycolysis in autolysis. This protein does not play much role in the taste of fish meat [4]. Heme proteins (hemoglobin and myoglobin) and enzymes (TMAO-demethylase and proteolytic enzymes) are included in this type of protein and if they are still contained in surimi processing, they will inhibit the gel formation process because when the myofibril proteins are heated, the sarcoplasmic proteins will be denatured and attached to myofibril proteins [5].

2.2 Connective Tissue Protein

This protein is often called the stroma and is almost insoluble in water or salt solutions but can be soluble in alkaline solutions. Binding tissue proteins are mostly found in myosepta and endomyosin, but some are found in the sarcolemma or other body parts but in small amounts. Collagen is one of the connective tissue proteins. If collagen is heated in water it can turn into gelatin. Collagen is composed of amino acids that make up protein, but collagen does not contain tryptophan, cystine and cysteine. Sometimes methionine and tyrosine are also present in small amounts. In this protein group, collagen is the dominant protein both in number and in its role. Collagen structure resembles mesh threads [4],[5].

The stroma group in fish is not many in number, its role is also not as big as the stroma in the meat of land mammals which plays a major role in the texture of the meat. The total amount of stroma in fish meat is approximately 6% of the total protein in fish meat. Connective tissue protein does not play a role in the formation of the surimi gel and the gelatin formed can inhibit the myofibril protein gel formation process and accumulate in one part of the product [4],[5].

2.3 Myofibril Protein

Myofibril proteins are proteins found in meat threads (myofibrils and myofilaments). Included in this protein group are the types of globulin protein groups such as myosin, actin and tropomyosin. This group of proteins plays an important role in the contraction and relaxation process of fish meat. The amount of protein in this group is approximately 50% of all existing proteins and is difficult to dissolve in water [4].

Actin and myosin are the main members belonging to the class of proteins that are soluble in salt solutions with a concentration of 0.05 – 0.5%. In fish meat, the amount of actin is about 15-25% while myosin is about 50-60% while tropomyosin is about 3-5% of all proteins of this group. Actin and myosin are labile proteins and can form more complex actomyosin. Actomyosin plays an important role in gel formation which is influenced by heat, fish meat texture and is insoluble in water but soluble in approximately 1% NaCl salt solution [4],[5].

3. SURIMI

3.1 Surimi Ingredients

To produce surimi of good quality will depend on many factors such as the type of fish, freshness level, fishing method, fishing season, growth phase and fish size. After that, the handling of surimi raw materials must be carried out properly, starting from the ship to the surimi processing place, everything is done in a cold chain and with maintained environmental sanitation and hygiene. [6] asserts that using old fish will make it more difficult to drain the water after washing the mashed meat. Regardless of the species, freshness is the most crucial component for raw materials to be turned into surimi, according to [7].

Other materials needed in surimi processing are ice, salt, cryoprotectant (sorbitol, sucrose) and other materials to increase water holding capacity (polyphosphate). Ice is used to keep the fish meat cold (low temperature) in order to avoid or inhibit the decrease in the quality of the freshness of the fish meat. Salt is usually used when washing mashed fish meat with cold water. The addition of salt is intended to accelerate the reduction of

water, the removal of mucus, blood and other impurities from the minced fish meat. The salt used should be clean, white and fine table salt as much as 0.2-0.3% of cold washing water [2].

3.2 Surimi Production

The basic principle of making surimi is that the fish meat is taken, cleaned of unwanted materials (bones, scales, skin, etc.), minced, washed and part of the water content removed, if it will be stored in a frozen state then the surimi is added to the ingredients. Anti-denaturation (cryoprotectant), all stages of making surimi are better done in a room with a low temperature (cold chain) or can also use ice at each stage of processing fish meat.

Fish Gutting

Surimi production begins with the process of eviscerating and cleaning the fish from all types of dirt. The head and entrails of the fish were removed, the scales were removed and washed. Gutting must be done carefully so that the contents of the stomach do not contaminate the fish meat to be made surimi [2]. Therefore, the place / table, weeding equipment must be kept clean. The head and entrails of fish contain a lot of fat and protease enzymes, besides that contamination of fish entrails will affect the appearance of the final product because it causes the color of surimi and its derivative products to be darker.

Meat Separation

The next stage is the separation of fish meat which can be done manually using a filet knife or mechanically using a meat separator. For types of fish that contain red meat, the red meat is separated first so that white fish meat is obtained. This red meat contains a lot of *haem* pigment which can adversely affect the color, odor and aroma of surimi. *Haem* pigments or heme proteins such as myoglobin and hemoglobin in addition to causing a dark color can also increase the risk of fat oxidation which will end in rancidity [2],[8]. If you are going to use the filleting method, then the fish skin must be separated because this part is very rich in collagen, fat, and the particle size is large so that later it will interfere with the ability of surimi gel formation.

Minced Meat

Fish meat that has been cleaned of all kinds of dirt and skin is then mashed using a meat grinder (meat extrude or grinder). If the meat separator is used at the stage of separating the meat, then apart from the bones and skin being separated, the fish meat produced will be directly in the form of mashed meat.

Washing

The resulting mashed meat is dark in color because it still contains fat, residual blood and other sarcoplasmic proteins. To separate these components, the mashed meat is then washed using clean cold water at a temperature of $1^{o} – 5^{o}$C with a volume of water 5-10 times the volume of mashed meat. During washing, the mashed meat is stirred until homogeneous with a washing cycle of 2-5 times. However, the volume of water and the number of wash cycles are highly dependent on the type of fish, the level of freshness, the type of washing equipment used, and the desired final quality of the surimi. In general, in the washing process a mixture of NaCl and $CaCl_2$ salts is added to facilitate the removal of water at a later stage [2],[8].

Washing with cold water is the most important step in the production of surimi because it will be associated with the removal of sarcoplasmic proteins that are soluble in water or salt solutions with low ionic strength as well as to ensure maximum gelling ability. Sarcoplasmic protein content in fish actually varies but in general it is higher in pelagic fish than demersal fish [6].

In this process, dissolved nitrogen components, blood, pigment, fishy aroma and fat that can inhibit gel formation will be removed. Meanwhile, myofibrillar protein becomes concentrated so that the ability to form a gel also increases. During this process, salt can also be added so that the reduction of water from mashed meat goes faster [2],[6].

Water Removal

The water that is still contained in the surimi after washing should be removed as much as possible, up to 80-82% or the equivalent of fish fillet [8]. Water removal can be done by pressing the mashed meat in a filter cloth or by using a screw press and centrifuge.

Surimi which has been removed from the water is then purified/refined using a strainer/refiner, the process is called straining/refining which aims to remove the remaining skin, bones and small spines so that the surimi mashed meat is clean, white and odorless. The principle of this tool is similar to the meat separator, namely the meat

is pressed through a hollow cylinder with a smaller diameter than the meat separator machine, namely 1-3 mm [2]. This step can also be carried out before the last water removal.

Cryoprotectant

Cryoprotectant is used to inhibit the protein denaturation process during freezing and frozen storage. The addition of this substance is important to ensure the functional properties of frozen surimi considering th at freezing can cause denaturation and aggregation. The amount added is about 3-5%. Materials that are often used as cryoprotectants are carbohydrates with low molecular weights such as sucrose. Sorbitol is also commonly used and is the strongest cryoprotectant. The addition of sucrose alone without sorbitol will result in surimi becoming sweet and changing its color during freezing [6],[8].

A cryoprotectant must have a molecular structure that has one important (essential) group –OH, -COOH, or $–OPO_3H_2$ and more than one complementary group, -OH, -COOH, $-NH_2$, -SH, $-SO_3H$ and/or $–OPO_3H_2$. Then the functional groups must have a suitable place and point to each other in an orderly manner. Finally, the molecular size of a cryoprotectant agent must be small enough [6],[9].

It is also known that the addition of cryoprotectant can increase the strength of the gel. Other ingredients are often added to surimi with the aim of improving the properties of surimi, especially its elasticity and softness, such as by adding 0.2-0.3% polyphosphate in the form of sodium tripolyphosphate salt or a mixture thereof with tetrasodium pyrophosphate (1:1) which will be synergistic with carbohydrates [2],[8]. According to [10], the strength of the surimi gel will increase with the addition of a phosphate mixture. Better enhancement is achieved by completely substituting sodium tripolyphosphate by phosphate mixtures.

The ingredients are mixed into the surimi using a mixer, silent cutter or grinder and the increase in temperature due to grinding must be avoided by using a machine equipped with a cooler or using ice cubes. It is very important to keep the mixing temperature below 13^oC [6].

Storage

After the surimi mixture is homogeneous, then the surimi is molded into a square shape. The trick is to put the surimi into a pan (mold) and then compact it. Usually, commercial surimi is packaged in 10 kg/block with a thickness of 60mm in polyethylene bags. Surimi in block form is then frozen in a contact freezer (with a temperature below -35^oC) or using an air blast freezer (-25^oC to -30^oC, for 3 hours). After frozen, the surimi is removed from the pan, put in two cardboard boxes, labeled and stored frozen (-20^oC to -30^oC). If the processing is carried out properly, freezing goes quickly and storage meets the requirements (no temperature fluctuations) then frozen surimi can last up to one year [2],[6].

4. SURIMI GEL FORMATION

The theory of gelling from fish muscle proteins that have undergone mincing and washing shows that a high concentration of salt (NaCl) is required to dissolve myofibril proteins, especially myosin and actomyosin. This protein can form a gel during heating due to denaturation, interaction and aggregation [11]. Myofibril proteins have a reactive surface after the protein is unfolded or denatured. During heating of surimi paste containing salt, the protein chains will open and reveal the reactive surfaces of adjacent proteins. Then these chains will interact to form intermolecular bonds. When sufficient bonds occur, a three-dimensional network is formed to produce a gel. In this process there are four types of chemical bonds that play a role and can bind proteins. These four types of bonds are hydrogen bonds, ionic bonds, hydrophobic interactions and covalent bonds [5],[12].

Hydrogen bonds are weak dipole bonds and do not play a role in gel formation but play an important role in stabilizing bound water in hydrogels. Ionic bonds are bonds that attract each other positive and negative charges on the surface of the protein and cause myofibril proteins to aggregate and not dissolve in water. In the manufacture of surimi, to increase the solubility of myofibrils, salt is added because salt ions will bind to groups that have op posite charges on the protein surface. The formation of ionic bonds only in surimi paste will not affect gel formation. Covalent bonds are formed by sharing electrons and are not easy to break once formed between proteins. Most of these types of bonds are not sensitive to temperature. During heating at a temperature of more than 40oC disulfide bonds (S – S) are the most commonly formed covalent bonds. A disulfide bond is formed as a result of the oxidation of two cysteine molecules to produce a sulfhydryl reactive group [5],[12].

The strength of the bond or hydrophobic interaction will increase with increasing temperature up to almost 60^oC. The formation of hydrophobic interactions between protein molecules in addition to the formation of disulfide bonds which also occurs during heating, is thought to be the main mechanism of surimi gel formation. Proteins have hydrophobic groups on the inside and hydrophilic groups on the outside. When the protein is denatured (by the heat

of the water) or unfolds the chain, the nuclei of the hydrophobic groups will open and touch the water. Water molecules close to the hydrophobic groups become oriented to form clathrates with hydrogen bonds. This arrangement will reduce the rate of movement of water molecules. To minimize protein contact with water and make the system more stable to heat, the hydrophobic part of the protein will approach each other (associate) with other hydrophobic parts. This association results in effective binding through hydrophobic interactions between proteins and proteins so that the formation of a gel network will occur [5].

4.1 Setting and Gel Suwari

Surimi's ability in setting is thought to be the result of the formation of non-disulfide covalent bonds catalyzed by enzymes between protein molecules. This bond is formed between the amino acids glutamine and lysine which is located in adjacent protein chains as a result of the activity of the enzyme transglutaminase (TGase) which is contained in fish muscle. Hydrophobic interactions between protein molecules also play an important role in setting reactions at low temperatures. The addition of salt to surimi paste can also support the role of hydrophobic interactions because some types of salt such as sodium chloride will react with water molecules to strengthen the hydrophobic interactions between proteins. Setting will take place better at a higher pH and requires dissolving the protein by salt first. Salt will destabilize the protein, causing more available groups to form dipeptide bonds by TGase and the formation of hydrophobic interactions. The optimal setting temperature and time will depend on the type of fish, sex, harvest season, fishing grounds, and ambient water temperature [5].

When surimi paste that has been added with salt is stored at room temperature, the thick surimi paste will lose its viscosity and turn into an elastic gel that can no longer be molded into the desired shape. This phenomenon is called suwari (setting) and is undesirable in making surimi. However, in the end it was found that surimi paste which was subjected to the suwari process under controlled conditions resulted in higher gel strength in surimi after cooking compared to surimi paste which was cooked immediately. Setting at low temperature is carried out at a temperature of 5^{o} - 32^{o}C while setting at high temperature is carried out at 32^{o} - 43^{o}C. The mechanism for the occurrence of suwari includes changes such as:

a. Increased protein hydration as a result of the addition of salt ions.

b. Denaturation or transformation of proteins

c. Formation of cross-links that bridge between protein molecules.

It is further known that the crosslinking of myosin is caused by the activity of transglutaminase contained in fish muscle and plays a role in the formation of suwari [9]. During setting, the myosin heavy chain polymerizes through the formation of non-disulfide covalent cross-links catalyzed by endogenous transglutaminase enzymes (Benjakul et.al., 2004). The results of [13] research found that there were protein degradation products at the setting at 25^{o}C, while the setting at 40^{o}C showed even more degradation products.

4.2 Modori

Suwari gel formation takes place at a temperature of more than 50^{o}C at the time of heating. However, when this gel exceeds 60^{o}C, some of the structure of this gel will be destroyed. This event is called a modori. There is a hypothesis which states that modori is caused by proteases. Alkaline proteases which are active at 60^{o}C are found in fish meat. However, some research data contradict this hypothesis, that proteases are strongly inhibited by ±0.5M salt and in the fact that modori does not occur when this enzyme is added to fish meat paste [6].

The elastic, non-transparent kamaboko gel forms when meat paste is heated after passing through the modori temperature range. The protein configuration is changed by heat to form an interaction of radical groups on the surface of the molecule which then forms a network that is stronger than the Suwari gel network. The intermolecular bonds that form the structural network are known as the role of hydrogen bonds and hydrophobic bonds [6].

Modori is an undesirable phenomenon in kamaboko processing where the gel strength of the product is damaged during the heating process. Modori can be translated as "return" in Japanese because the elastic gel that has formed will return to its original inelastic form. This can occur when heating surimi is carried out with a temperature increase that is too slow in the temperature range of 50^{o} - 70^{o}C for a longer time than the heating speed in general, and a very brittle gel is formed. The cause has been identified as a result of the proteolytic degradation of fish myofibril proteins by a group of heat-resistant protease enzymes. The nature of this modori formation is very specific depending on the protease activity of each species [9],[12].

Modori formation can be inhibited by the addition of sugars such as glucose, fructose and sucrose; dry egg albumin, alcohol and protease enzyme inhibitors (beef plasma protein, egg white, whey protein, potato extract) [12],[14].

5. SURIMI-BASED PRODUCT

5.1 Kamaboko

Kamaboko is a typical seafood from Japan in the form of a homogeneous protein gel and is used to represent a group of traditional foods derived from surimi raw materials. The washing process, mixing with salt and heating are the three basic steps in kamaboko processing. The characteristic of kamaboko is its elastic texture which is known as ashi. An important component in the formation of *ashi* is actomyosin contained in fish meat. Therefore, denaturation of actomyosin must be prevented and components that would hinder the formation of *ashi* must be removed [6],[15].

So far, fish meat that has been mashed, reduced in size and has gone through the washing stage is indispensable for making kamaboko. This can be ascertained based on the number of cross-links which will form a strong protein network structure in a gel made from minced meat that has been mashed and passed through the washing step [16].

5.2 Surimi Imitation Products

Various efforts were made to develop new products made from surimi starting from 1974 until now. This is mainly due to various regulations regarding pollution, fishing, and the scarcity of fish raw materials which has caused the price of some fishery raw materials and frozen surimi to rise. In addition to new surimi products, new technologies, waste treatment, utilization of other fish species, and methods for preserving surimi-based products are also being developed. One of the most developed products is the analog crab leg which was created in 1975, the principle is by slicing kamaboko blocks into rope shapes and then further processing with addition by surimi paste then extruded into crab legs shape, heated and cut into pieces small and flavorful. In addition to analog crabs, scallops and shrimp analogues were also developed which turned out to be successful in the market [15].

6. CONCLUSIONS

Important functional traits of surimi include its propensity to gel and its capacity to store water (water holding capacity). Freshwater or marine fish can be used to make raw surimi. Because it is readily available and has the capacity to produce the right gels, tilapia has been employed as a raw material for the creation of surimi. Actomyosin, which is insoluble in water but soluble in a salt solution containing about 1% NaCl, plays a significant role in the development of gels that are impacted by heat and the texture of the fish meat. To produce high-quality surimi, it is necessary to have knowledge of fresh fish raw materials, protein properties, the effects of washing, adding salt, adding additives like cryoprotectants, and the effects of storage on the product. Only then can we produce final processed products that are in line with customer demands and can still be accepted by customers if we want to sell it. Freshness is the most important factor for turning raw materials into surimi, regardless of the species. Ice, salt, cryoprotectants (sorbitol, sucrose), and other elements to boost water holding capacity are additional resources required in the preparation of surimi (polyphosphate). The fundamental process for manufacturing surimi includes taking the fish meat, cleaning it of any impurities (bones, scales, skin, etc.), mashing it, washing it, and removing some of the water. If the finished product will be frozen for storage, the surimi is then added to the other ingredients.

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