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Weak Acid-Induced Gel from Shark Meat and its Food Applications

V Venugopal[1,2]*

[1]*Former Head, Seafood Technology Section, Food Technology Division, Bhabha Atomic Research Center, Mumbai, India*

[2]*Visiting Faculty, Department of Food Science and Technology, Kerala University of Fisheries and Ocean Sciences (KUFOS), Kochi, Kerala, India*

***Corresponding Author:** V Venugopal, Former Head, Seafood Technology Section, Food Technology Division, Bhabha Atomic Research Center, Mumbai and Visiting Faculty, Department of Food Science and Technology, Kerala University of Fisheries and Ocean Sciences (KUFOS), Kochi, Kerala, India.

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Abstract

Shark species are valued essentially for their fins, which are used for the preparation of exotic soups. Shark meat has limited consumer appeal essentially due to its unappealing flavor. Therefore, fishermen usually cut off fins from live sharks immediately after they are caught, and discard the finless animal back in the ocean. This article points out a novel process for utilization of shark meat for food product development, making use of its gel forming properties under mild acidic conditions. Washed shark meat suspended in water undergoes gelation in presence of traces of weak acid giving rise to a thick viscous mass of gel. The gel consists of water entrapped in the protein matrix. The gel mass can be converted into protein-rich food products employing different processes. Some of them include restructured products such as imitation items like fillets, battered and breaded (coated) products, sausages, extrusion-cooked products, among others. The gel can also be used as a binder in food formulations, and also in aqua-feeds. Besides, lactic acid fermentation of the gel can give hygienic sauces. These possibilities suggest potential to enhance consumer acceptance of shark meat. Recent interests for low-fat, low-sodium and functional foods may encourage utilization of shark meat for food product development.

Keywords: *Shark Meat Structural Proteins; Myosin; Mild Acid Gelation; Product Development; Restructured Foods; Value Addition*

Abbreviations

Chondrichthyes: A class of vertebrates, whose skeleton is characterized by internal skeleton of rubbery cartilage rather than true bone; Chondrocytes: Cells found in cartilage, involved in maintenance of the cartilage; FAO: Food and Agriculture Organization of the United Nations, Rome, Italy; Food Extrusion: Process in which a mixture of ingredients are forced through a barrel under elevated temperature and pressure, followed by shaping the cooked food with suitable die at the end of the barrel; Elasmobranchii: Subclass of Chondrichthyes, and includes Sharks, Rays and Skates; EPA: Eicosapentaenoic Acid, (C20:5), Polyunsaturated Fatty Acid (PUFA); DHA: Docosahexaenoic Acid, (C22:6), Polyunsaturated Fatty Acid (PUFA); Shark: Carnivorous Fish with Cartilaginous Skeleton; Surimi: washed wet concentrate of myofibrillar proteins from raw minced animal flesh, including fish; Transglutaminase: Protein-Glutamyl Transferase (EC 2.3.2.13), catalyzes protein cross-linking

Introduction

Sharks, rays, and skates belong to Chondrichthyes (sub-class, Elasmobranchii). Sharks are ecologically and demographically diverse. Some of the commercially important species of shark include short fin mako, scalloped hammerhead, smooth dogfish, spineless dogfish,

big-eye thresher, pelagic thresher, sandbar, white, and dusky sharks [1,2]. Global catch assessment estimates that approximately 1.41 million metric tons of sharks were landed annually during the period 2000-2010; in the year 2011, landing of 8,05,644 metric tons of Chondrichthyes has been reported [3,4]. Sharks are sources of products such as fins, leather, gills, teeth, oil, and cartilage [3,4]. Of these, fins, perhaps, are the most valued, which are used for exotic soups, particularly in Asian countries. Fins from shark species such as black tip, blue, hammerhead, sandbar, and white tip, mako are commonly collected. Fishermen, usually, cut off fins from live sharks immediately after they are caught, and discard the finless animal in the ocean Shark fins are marketed in many forms, namely, skin-on, skinless, with cartilage, wet, salted, dried, smoked, cooked, frozen, and others [3]. The FAO statistics conservatively put average total value of world shark fin imports at US$ 377.9 million per year during the period 2000 to 2011 [3]. The extensive hunting of sharks for their fins has resulted in overexploitation of the species. The problem is compounded by the low reproductive rates of sharks and slow growth of siblings to reach maturity. According to the International Union for Conservation of Nature, 64 shark species are endangered needing protection, and 514 species are in need of improvements in their fisheries [5].

Apart from the fin, other commercially important products from shark include leather, teeth, gills, cartilage, and oil, among others. Shark fin cartilage is a connective tissue, which consists of chondrocytes and a complex extracellular matrix consisting of the proteins, collagen and elastin, and also proteoglycans. Shark cartilage is used in many pharmaceutical preparations, as are other parts of sharks such as ovaries, brain, skin and stomach [6]. Chondroitin sulfate (CS) is a key functional component of shark cartilage, which is widely used to treat arthritis. Derivatives of CS also have significant medicinal value [7]. Leather from large sharks is used for bags and shoes, while shark teeth find applications in dentistry. Collagen and gelatin are valuable ingredients in cosmetics and food processing [8]. Another major by-product is the shark liver oil. The liver of shark comprises 22 to 30% of body weight and the oil may be as high as 90% of the liver [9]. The liver of five dominant shark species in the Indian Ocean showed 26 - 60% oil contents. Triacyl glycerol was the predominant lipid class (65.2 - 86.1%) in all the species followed by sterol esters (2.9 - 12.7%), and hydrocarbons (2.5 - 11.6%) [10]. Shark liver oil is a good source of omega-3 polyunsaturated fatty acids (PUFA), particularly eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), which are known to provide health benefits [9,10]. The oil has also appreciable content of the hydrocarbons, squalene and pristane, and also fat soluble vitamins [9,10] oils from liver of black shark, Mako shark, and hammerhead shark are rich in vitamin A and D contents [11]. The oil extracted from the liver of the deep sea shark, *Echinorhinus brucus* showed *in vitro* cytotoxic effect against the human neuroblastoma cell line [12].

Shark meat

Shark meat, unlike the products discussed above, has limited consumer acceptance. This may be attributed to the peculiar flavor of the meat, essentially due to its exceptional contents of urea and trimethylamine oxide [13,14]. Shark meat is consumed mostly in countries such as China, Taiwan and Japan. The meat is gaining popularity, particularly Italy and Brazil. North American and European markets such as the USA, Italy, and France seem to have a preference for sharks belonging to the dogfish species [3]. Consumption of shark meat in many countries has shown at least marginal increase over the last decade. According to FAO an amount of 121,641 metric tons worth US$ 379.8 million of chondrichthyan meat were imported in 2011, representing an increase of 42% by volume compared with that in 2000 [3]. The increase in consumption of shark meat is probably driven by the general demand for seafood, and also due to regulations prohibiting dumping of live animals in the sea after removal of their fins [3]. The current scenario therefore demands processes for value addition of shark meat to encourage its utilization as food all over the world. This article discusses novel gel forming properties of shark meat and its uses for value addition of the meat. At the onset characteristics of shark muscle and the muscle proteins will be briefly mentioned.

Characteristics of shark muscle

Raw shark muscle contains 74 - 78% moisture, 20 - 22% proteins, and 1 - 5% fat [14]. While the liver of shark is rich in oil, its muscle has very little lipid content. The muscle tissues of the deep sea shark species including Portuguese dogfish, black dogfish, leaf scale gulper shark, greater lantern shark, small eyed rabbit fish/ghost shark, and bird beak dogfish had less than 1% fat. Their lipids carried

docosahexaenoic acid (DHA), (C22:6n-3) as the major omega-3 polyunsaturated fatty acid (PUFA). The lipids had also a good proportion of arachidonic acid (20:4n-6) [15]. Shark meat is a good source of vitamins such as niacin, vitamin B6, and vitamin B12, and minerals, phosphorus and selenium [16]. Shark muscle has unusual presence of urea and also trimethylamine oxide (TMAO). In Elasmobranchii such as skates and dogfish, urea content is as high as 1500 to 2000 mg in 100 g muscle [14]. Urea is used as an osmolyte by the animal. The compound is also having other less-understood roles in the biochemistry and physiology of the muscle [17]. Besides urea, significant amount of hydroxyl urea has been reported in Elasmobranchii [18].

Ice storage of shark meat results in the leaching of urea and other soluble nitrogen compounds. Urea content in the shark, *Scoliodon laticaudus*, was reduced by 25% during 12 days of ice storage. This was associated with two-fold increase in total volatile base nitrogen including trimethylamine (due to bacterial reduction of trimethylamine oxide), responsible for off-odor at the end of ice storage. Solubility of proteins showed an initial increase reaching a value up to 88%, which reduced after 12 days of ice storage. Prolonged chilled storage also caused aggregation of proteins and adversely affected viscosity and emulsion capacity of the proteins [19]. Total volatile base, trimethylamine, urea and ammonia contents increased during 12 days of ice storage of white cheek shark [20].

Shark meat proteins have appreciable functional and nutritional properties. Functionally the proteins have fairly high water absorption capacity, which can make their use as additive in bakery and meat products and pastes [21]. Shark proteins have an amino acid score (AAS) as high as 125, indicating their high nutritional quality [16]. The dogfish shark muscle proteins have all the essential amino acids, and high protein efficiency ratio (PER) values, making them potential dietary protein supplements [22]. Table 1 gives typical functional properties performed by fish muscle structural proteins, which are valuable in food product development.

Functional property	Mode of action	Product
Solubility	Protein solvation	Dispersion, soup
Water absorption and binding	Entrapment of water in the protein matrix	Surimi, surimi-based products, sausage, fish balls
Viscosity	Thickening	Gravies, soups
Gelation	Protein matrix formation, entrapment of ingredients in the protein matrix	Surimi, surimi-based products, sausage, patties
Cohesion-adhesion	Adhesion	Surimi, surimi-based products, sausage
Elasticity	Disulfide bonds	Surimi, surimi-based products, sausage
Emulsification	Formation of fat emulsion, fat binding	Sausage, fish balls, soup
Flavor-binding	Adsorption, entrapment, release	Seafood analogs

Table 1: *Typical functional properties of fish muscle structural proteins and their applications.*

Gelation of fish muscle proteins

Nature of fish muscle structural proteins

The proteins of fish muscle, including that of shark, can be grouped into three fractions, namely, sarcoplasmic proteins (20 - 30% of total proteins) consisting of myoglobin, hemoglobin, globulins, albumins, and various enzymes; the stroma proteins consisting of collagen and gelatin; and, the structural proteins or myofibrillar proteins. Sharks and other Elasmobranchii contain up to 10% of stroma proteins, in comparison to up to 3% stroma proteins in teleost muscle. Myosin, which constitutes 50 - 58% of the myofibrillar proteins, is the major structural protein of the muscle. Other structural proteins, which are in small proportions, include actins (F and G types), and the regulatory proteins, tropomyosin and troponin. The structure of myosin molecule consists of two heavy chains of 200 and 240 kilo dalton (kD), which are associated non-covalently with two pairs of light chains of 16 to 28 kD. The myosin molecule resembles a thread (2 nm x 160

nm) with two globular heads (19 mm) attached at one end to a tail portion. Compared to vertebrate myosin, fish myosin is more sensitive to denaturation, coagulation, or chemical changes. The fish myofibrillar proteins have poor solubility in water [23,24].

Gelation of myosin and other myofibrillar proteins

Ability to form gel is an important functional property of macromolecules including proteins. A protein gel is an intermediate form between solid and liquid phase. The gel structure consists of strands of protein chains that are cross-linked to form a continuous three-dimensional network, entrapping water in the matrix. Of all the known proteins, myosin is the most capable to undergo gelation [23]. Research in gelation of myosin was encouraged with the recognition of potential of the gel for the development of surimi-based products. Surimi is a wet concentrate of high-quality myofibrillar proteins, predominated by myosin, which is obtained after repeated washing of fresh fish mince. The washing process removes low molecular sarcoplasmic compounds from the fish meat, which is essential to prevent intervention of the compounds with the gelation of myosin. The washed meat is solubilized in sodium chloride (usually at O.6M), and then incubated overnight at 0^{o} to 4^{o}C, or subjected to mild heat (40o - 50^{o}C) for several min. Under chilled conditions gelation takes place at much slower rate. The gel set at low temperature is weak and possesses high elasticity and transparency. Mild heating at 40^{o} - 50^{o}C enhances the gelation process. Surimi initially set under mild heat conditions gives a stronger gel if subsequently heated to 80^{o} - 90^{o}C, due to enhanced cross-linking of the proteins [23,24].

Gelation of myosin essentially involves three steps viz., dissociation of myofibril structure during protein solubilization in the presence of salt, unfolding of myosin structure induced by heating, and irreversible aggregation of unfolded myosin to form a three-dimensional structure. During aggregation head portions of myosin molecules interact through disulphide bonds when helix-coil transitions take place in the tail parts of the molecules. The bonds involved in stabilisation of the gel structure include both covalent (disulfide) and non-covalent (hydrophobic, hydrogen bonding and electrostatic) linkages [24-28]. During the aggregation process water, oil and flavour compounds may be entrapped in the gel matrix, which is of importance in the development of food products. Thus, the rigidity of the gel could be suitably adjusted by incorporating ingredients such as salt, starch, polyphosphate or proteins from other sources in the matrix [24-28]. The myosin gel, therefore, is a base for the manufacture of a variety of foodstuff, such as the traditional Japanese kamaboko, and imitation shellfish products such as crabsticks, crab legs, crab meat, scallops, among others, which have good demand in global markets, particularly in Japan, the US and Europe [24,29]. Meat from a number of fish items has been examined for their gel forming ability with a view to use their surimi for food product development. Of various fish items, Alaska pollock has been recognized ideal because of low fat content and whitish-color of the meat, and visco-elastic nature of the gel [24]. Reports about surimi from sharks and rays are rather scarce. Some shark species examined in this respect include thornback ray (*Raja clavata*), and angel shark (*Squatina* spp.) [29,30].

Gelation of shark myofibrillar proteins under weak acidic conditions

As discussed above, gelation involves unfolding and aggregation of protein moieties. Unfolding of the native myosin during conventional gelation is brought about by salt solubilization and mild heating. Logically, gelation should also be possible if the protein is made to unfold under controlled, non-thermal conditions in the absence of salt. Slow lowering of pH by acidulants such as weak acids under ambient conditions can cause protein unfolding [31]. The proteins that unfold as a result of mild acidification can aggregate among themselves to form the gel. The aggregation can be accelerated if the acidified proteins are subjected to mild heat treatment, as in the case of surimi-type gelation. Inorganic acids cannot be used since they bring about drastic fall of pH causing precipitation of the proteins. The advantages of the gelation under acidic conditions are mainly two. There is no need of salt to dissolve the myosin as in the conventional surimi type gelation, which offers scope for consumer-friendly salt-free (or low sodium) products. Secondly, because of the acidic nature, the gel is comparatively resistant to microbial spoilage and hence has better shelf stability.

Process of making weak acid induced gel from shark meat

The process of mild acid-induced gel formation from shark meat involves three steps, namely: (i) initial washing: for this shark meat are cut into 4 to 5 g pieces, held overnight in twice its volume of cold (5o - 10°C) potable water, decanting off the wash water, and rinsing of the meat in fresh water, (ii) homogenization: the washed meat are homogenized in equal weight of fresh water, (iii) gel formation: to the homogenate of the washed meat in water acetic acid or vinegar is added drop-wise while gently stirring to reduce pH of the slurry from 6.5 to 4.0. Gel formation is indicated by increase in viscosity of the homogenate, parallel with the fall in pH due to acidification, as shown in figure 1. The acidified slurry is left for 3 hrs at ambient temperature to complete the gelation process. Alternatively, the acidified slurry can be heated to 50°C for 10 min for early completion of the gelation process. Gelation can be measured by viscosity measurement using Brabender viscograph. The gel formation is visible indicated by thickening of the slurry into a hard mass. Viscosity changes due to gelation are dependent upon the protein concentration. Presence of salts such as sodium chloride, potassium chloride and calcium chloride inhibited the low-pH-induced gelation of the proteins [32].

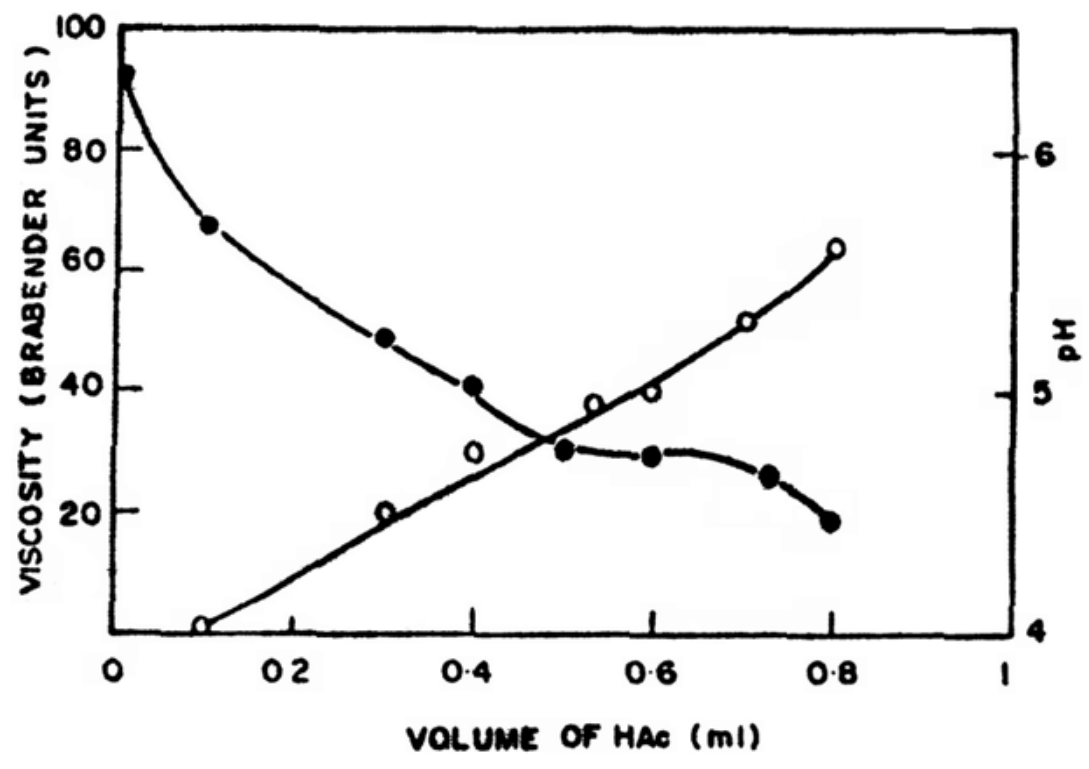

Figure 1: *Rise in viscosity against weak-acid induced lowering of pH during gelation of shark proteins. Acetic acid was added drop-wise to homogenate of equal amounts of washed shark meat and water. The viscosity change during acidification was determined by Brabender visco-amylograph. Reprinted from Venugopal., et al. (1985), with permission from Elsevier.*

As in the case of surimi, initial washing of shark meat prior to acidification is essential to remove the sarcoplasmic fraction, including urea, blood and myoglobin, which otherwise interfere with the gelation process. The washing step, besides removing these compounds, also makes the meat almost odorless and colorless. Removal of soluble compounds by washing treatment has been reported in the case

of white cheek shark muscle [20]. Another advantage of washing is that it enhances affinity of the structural proteins towards water. This has also been observed even in the case of the fish, Bombay duck (Harpadon nehereus), the raw muscle of which has moisture content as high as 90%. Holding the washed Bombay duck meat in 2% (v/v) acetic acid resulted in up to 33% (w/w) increase in weight due to hydration [33]. In the case of shark meat, gelation was associated with hydration of proteins, as indicated by significant imbibing of water in the protein matrix. The washed meat has also ability to absorb oil and hence has increased emulsion forming ability [34]. Figure 2 gives symbolic representation of structural changes and hydration of shark meat proteins during gel formation.

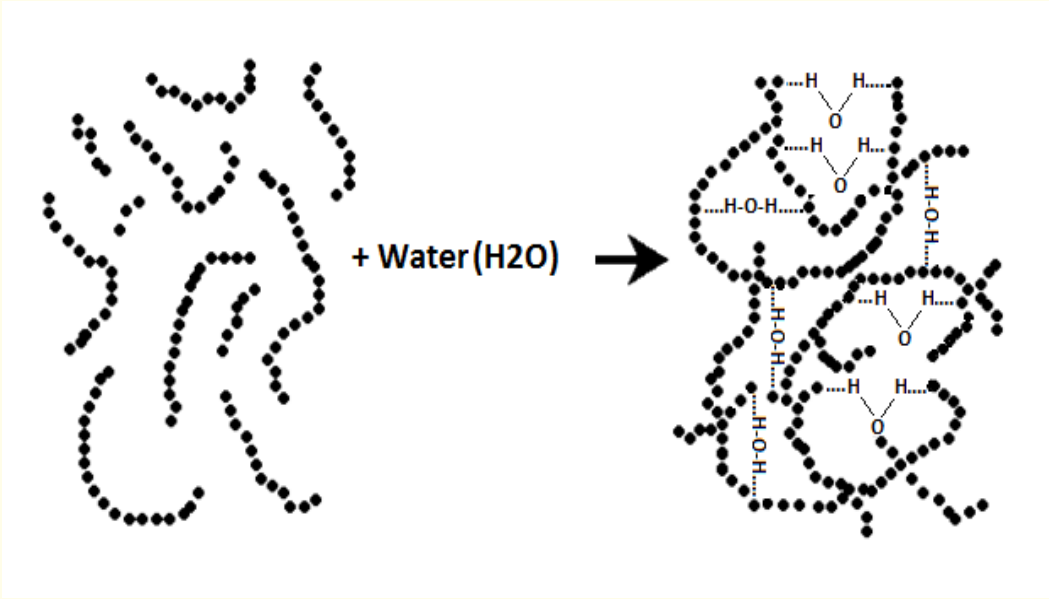

Figure 2: *Symbolic representation of structural changes and hydration of shark meat structural proteins under weak acid induced gelation.*

Characteristics of weak acid induced gel from shark meat

The gelation of shark meat is characterized by formation of thick mass of gel composed of water is entrapped in the protein matrix. Washed meats of several other fish species do not give such thick mass under comparable acidification conditions. The unique hardness of shark meat gel may be attributed, at least partially to its higher content of collagen, which along with its degraded product, gelatine influences interactions of proteins with water in the gel mass, leading to the hard consistency. The gelatine can also have a role in reduction of the rubbery texture of the final product [23]. The hardness (rigidity) of the gel depends essentially on the water content of the shark meat slurry. Variations in moisture from 85 to 90% can have significant effects on hardness of the gel, as shown in figure 3. It should be emphasized that whereas in surimi, the gelation is achieved by mild heating in presence of small amounts of salt, shark muscle does not require salt to undergo gelation under mild acidifications. In fact, presence of salt interferes with formation of electrostatic linkages during gelation and hence inhibits the gelation process [32]. The main features of conventional (surimi type) and mild acid-induced gelation are summarized in table 2.

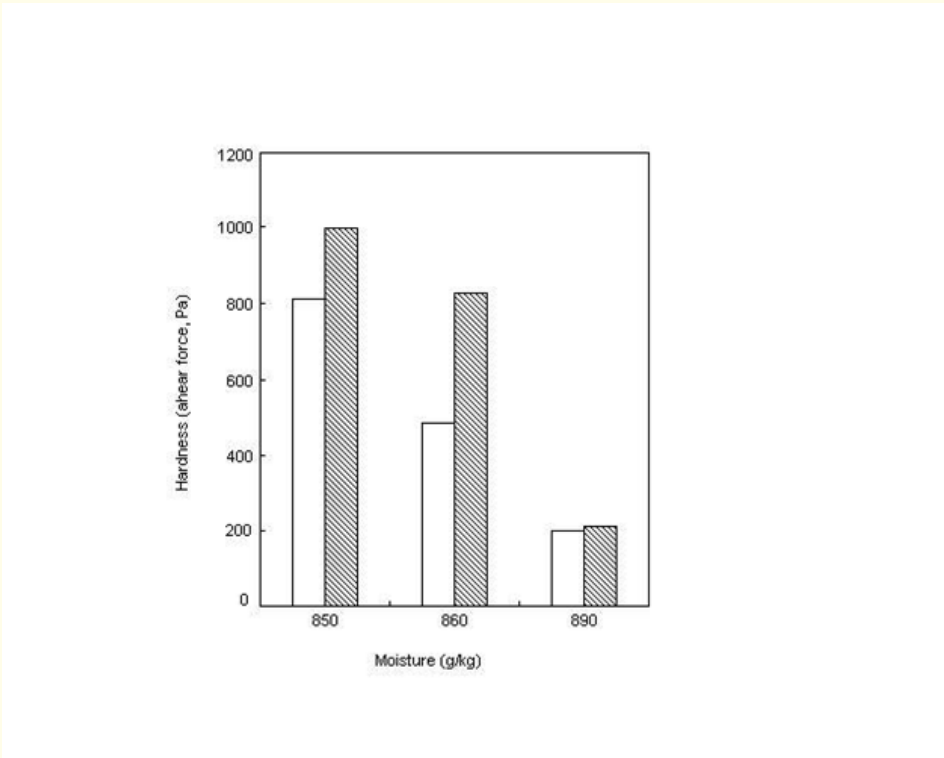

Figure 3: *Hardness of shark protein gel as a function of moisture content. Empty and filled columns indicate hardness values before and after open steaming the gel for 15 min, respectively.*

Characteristics	Conventional surimi gelation	Weak acid-induced gelation
Gelation pH	Neutral or slightly alkaline	Acidic pH (3.5-4.0)
Agents for gelation	Mild heat in presence of NaCl	Weak organic acids such as acetic or lactic acid
Chemical and structural changes	Hydration of proteins, Formation of covalent (disulfide) and non-covalent linkages leading to three-dimensional structure, degradation of myosin heavy chain, decrease in α- helix content and possible increase in hydrophobicity of myosin	Hydration of proteins, Formation of covalent (disulfide) and non-covalent linkages leading to three-dimensional structure, degradation of myosin heavy chain, decrease in α- helix content and possible increase in hydrophobicity of myosin
Water holding capacity of proteins	Excellent	Excellent
Oil emulsification capacity	Good	Good
Microbial stability of gel	Poor	Good
Rheological characteristics of gel	Visco-elastic nature	Visco-elastic nature reported only in hark meat gel
Influence of ionic compounds	Gel characteristics not affected	Adversely affect gel characteristics, protein precipitation

Table 2: *Comparison of conventional surimi gelation with weak-acid induced gelation.*

Apart from the changes in the three-dimensional structure of the proteins and associated entrapment of water in the gel matrix, other changes during gelation include reductions in the contents of myosin heavy chain and sulfhydryl groups of the protein. The gel formation of shark proteins is also indicated by changes in the dynamic visco-elasticity properties of the proteins. Shark protein gel showed higher storage modulus G' (a measure of elasticity or energy stored), than loss modulus, G" (a measure of viscosity, or energy lost). The G' increased with decrease in moisture contents suggesting higher rigidity of the gel at lower moisture contents. Relatively low values of tan δ (G"/G') indicated elastic nature of the gel [35]. In addition to dynamic visco-elasticity properties, the gelation was also measurable in terms of physical parameters such as the folding test. Ice storage of shark meat resulted only in marginal reduction of gel forming capacity [18,19]. It has also been reported that the gel forming capacity of washed shark meat can be enhanced by addition of the enzyme, transglutaminase, which catalyzes protein cross-linking [19].

Products from shark meat gel

Restructured products

Restructuring in food processing is conversion of food portions such as low value cuts and trimmings of red meat into products that resemble conventional or popular food items in their appearance, texture and flavor. The process involves homogenization of the food portions with food additives including preservatives, coloring and flavoring agents, followed by cooking the mixture, and shaping. The technology helps development of novel food items that can have better consumer acceptance, enhanced storage stability, and hence scope for value addition. The process for restructured beef roast, for example, involves one or more steps, viz. chunking, fiberizing, slicing, and tenderizing in presence of additives such as common salt, phosphate, alginate, lactate, pectate, among others. Restructured pork chops are prepared by grinding chilled raw pork trimmings in a twin-screw extruder and pressing the extrudate into meat logs of 8 - 10 cm dia. Machineries are available to disassemble the carcass and reassemble it in a way that gives it a texture similar to natural steaks, chops, and roasts. Restructured chicken is made by mincing of the raw material in presence of additives (binders) that hold the particles together and emulsify the oil present. Heat treatment of the mince gives the required texture. Additional processing steps may include breading, flavoring etc. Mechanical and functional properties of restructured meat products depend on the biochemical and physicochemical properties of muscle proteins, and also on the various binders incorporated. The technology has been discussed in detail [36].

Development of imitation products such as shrimp, crab sticks, lobster tails, etc. from surimi is the typical restructuring process in the area of seafood. The technology involves thorough chopping of surimi in presence of ingredients such as sugar, salt, binders, and flavors. The blended paste is shaped by passing through an extruder, followed by steam cooking of the shaped products. The process offers new edible products from both low-value fish species as well as filleting discards. Other commercially marketed restructured items include sausages, fish balls, cutlet, pate, patties, pastes, composite fillets, among others. Fish sausages are complex mixtures of muscle tissue, solubilized proteins, binders, fat, spices and water, which are stabilized as a result of emulsion formation by protein films. The mix is filled in casings, cooked and cooled. The products are vacuum packed to provide protection against oxygen and water vapor transmission. Sausages from mince of shark and also other marine fish such as tuna, marlin, and whale are manufactured in Japan. A number of restructured products have been developed from meat mince of fish such as silver carp, Mexican flounder, gilthead sea bream, mackerel, white croaker, squid, etc. Protein additives such as cereals, egg, and blood plasma are available as extenders to improve the functionality and processing yields and to reduce formulation costs of comminuted meat products. Their appearance may be improved by shaping the finished product in the forms of steak, chop or roast (in the case of red meat), and steak or fillet in the case of fishery products. Products may also be suitably tailor-made to satisfy regional interests. Consumer acceptance of restructured products depends upon composition of raw material, texture, flavor, appearance, potential health benefits, presence of natural ingredients, packaging etc.

Shark meat gel, prepared as discussed above, can be the raw material for restructured food items. The additives, required for the development of such products (preferably from natural sources) may be incorporated during homogenization of washed shark meat in water, prior to gel formation by acidification. Texture of the gel may be modified by incorporating small amounts of ingredients such as

egg white, wheat gluten, among others, while flavor can be enhanced by natural ingredients such as shrimp flavoring, and appearance by including natural colors such as carotenoids. As ionic compounds including common salt interfere with the gelation process, as mentioned earlier, salt has to be added only after the gelation process is complete. Nutritive value of the product can be enhanced by incorporation of vitamins, minerals and also various nutraceuticals. For making restructured fillets or steaks, the prepared gel is filled in heat resistant molds having desired shape of popular fish fillets or steaks, which are then subjected to open steaming for 15 min, followed by cooling to ambient temperature. The product can have texture comparable to normal fish steaks [37]. Figure 4 outlines process for the preparation of restructured shark products.

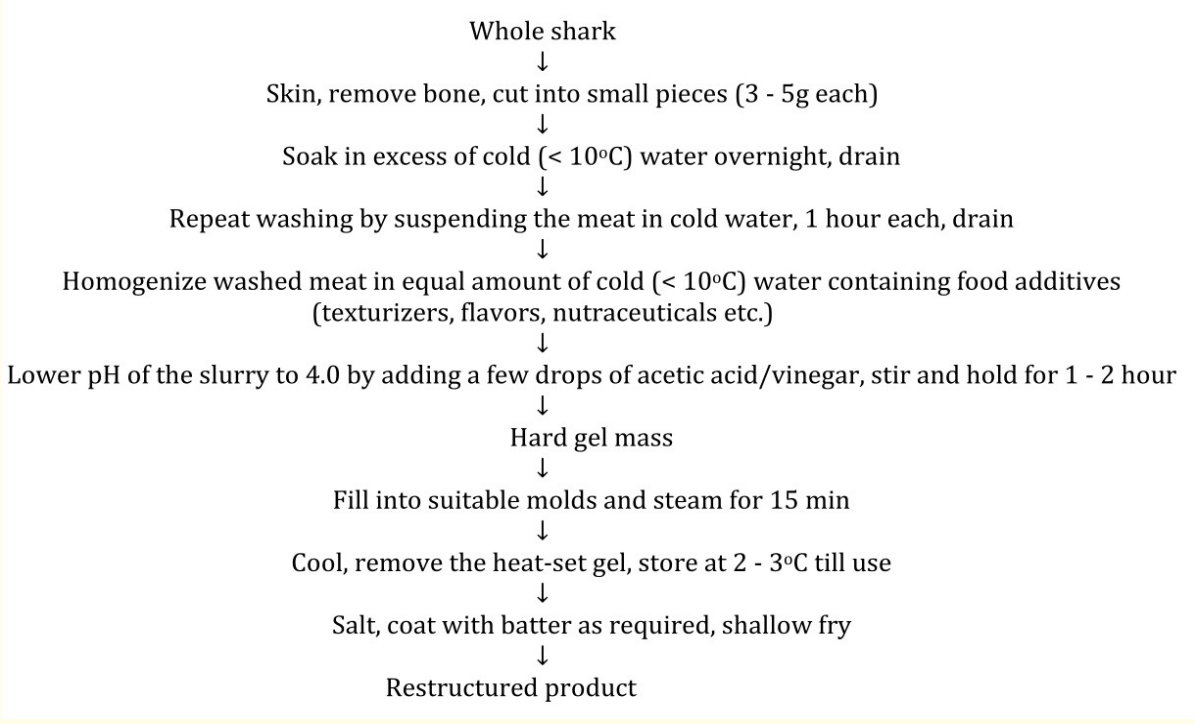

Figure 4: *General process for preparation of restructured shark protein gel products.*

The gel can also be used for composite fillets. Such fillets are usually made from smaller fish fillets, which are placed in a large fillet shaped mold in presence of some binders and compressed, with a low-pressure ram. After release of the ram, a fillet piece is obtained. Composite fillets could be made of shark meat gel along with mince or fillets from two or three fish species, in presence of appropriate polysaccharides as binders such as alginates, carrageenan, xanthan gum or pectin. The fillets, prepared in suitable molds, may be further processed by breading or marination [38]. The gel can also be used to develop imitation products like crabsticks, crab legs, shrimp etc., as in the case of conventional surimi. Products prepared from shark protein gel can have remarkable microbial stability due to mild acidic

nature of the gel, which prevents growth of spoilage causing microorganisms in the products. The storage stability also helps convenient marketing of the products. If required, before consumption, the products may be dipped in an aqueous solution of 5% each of sodium bicarbonate (baking soda) and common salt to remove the acidic nature and improve salt. The products are oil fried or grilled before consumption. Recent interests in low-fat, low-sodium and functional foods carrying nutraceuticals may create an increased market for restructured products [24].

Coated products

Coating by batter and bread crumbs has been extensively employed for value addition of fishery and other muscle foods, which form a sizeable portion of convenient foods [38]. The unit operations of coating include portioning/forming of the muscle food, pre-dusting, battering, breading, flash frying, freezing, packaging and storage. Pre-dust is a fine, dry flour (wheat flour, gums, and proteins, alone or in combination) that is sprinkled on the moist surface of the food portions to improve the adhesion of the batter. The traditional adhesive batter consists of flour and water, into which the product is dipped. The common ingredients used in batter are polysaccharides, proteins, fat/hydrogenated oils, seasonings, and water. Polysaccharides (wheat flour, corn flour, starch/modified starch and gums) provide viscosity, suspension-characteristics, texture and shelf life to the coated products. Proteins (milk powder, milk protein fractions, egg albumin, seed proteins or single cell proteins) improve water absorption capacity of the flour and thus increase the viscosity, while fat/hydrogenated oils contribute to flavor. Of the seasonings, sugar provides plasticizing effect, and improves the flavor through browning reactions; salt improves the taste and texture, and, spices enhance the flavor. The batter also incorporates a leavening agent such as sodium bicarbonate or tartaric acid to favor expansion of the product during frying. The bicarbonate can also help neutralization of any residual acid in the shark protein gel. The Tempura-type batters, which usually contain corn flour, form a crisp, continuous, uniform layer over the food, constituting its final coating. Breading is a cereal-based coating, often of breadcrumbs. The wider use of tempura batter in conjunction with coarse crumbs represents a new coating process for modern processing. Recent innovations in the coating industry relate to use of hydrocolloids such as methyl cellulose and hydroxypropyl methylcellulose to reduce oil absorption during frying, elimination of the frying step by microwave cooking, grilling, and sauce coating, among others [38-40]. Figure 5 indicates process flowchart for the production of coated products.

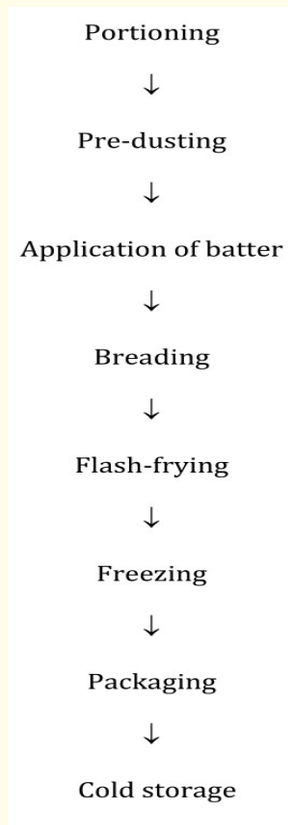

Figure 5: *General process flowchart for the production of coated products.*

Among the various coated seafood in the market, fish fingers, also known as fish sticks, are popular battered and breaded items prepared from fish such as cod, haddock or pollock. These were earlier prepared onboard fishing vessels using frozen skinless and boneless fillets of finfish. The process consists of salting the fillets in dilute brine to improve the color, taste and texture, and molding the salted fillets into blocks of standard size and weight. The blocks are kept frozen till used for coating. For coating, the frozen block is cut by automated cutting machines to sticks of desired shape and size, which are subjected to coating as discussed above. Fish mince from marine as well as freshwater fish can also be used for processing into a variety of coated products. Coated seafood products currently available in consumer markets include crustacean products such as coated shrimp, crab cakes and crawfish, coated mollusks such as clams, oysters, scallops, and squid. Some of the fancy items are coated butterfly shrimp, squid ring, stuffed squid rings, fish cutlets, and fish burgers. The coating technology showed further impetus with the development of surimi industry [38]. Table 3 gives benefits of restructuring and coating of food products.

Parameters	Benefits
Product characteristics	Provide desired texture, appearance, color, and flavor to food. Provides opportunity for novel products
Yield	Coating enhances yield including cooking yield
Storage stability	Provides structural reinforcement to the food and hence enhanced storage stability
Stability during handling	Improves stability during transport, frozen storage, microwave heating and other treatments.
Protection of the food	Coating provides a moisture barrier, which acts as food sealant by preventing natural juices from flowing out of the food
Nutritional value	Provides opportunity to incorporate vitamins, minerals and nutraceuticals in the food
Influence on bulkiness	Increases bulk of the food
Consumer value	Better consumer acceptance of products
Influence on cost	Reduces cost of the finished product
Marketability	Enhances marketability and hence economic value

Table 3: *Benefits of restructuring and coating of food products.*

The shark meat gel can be an interesting raw material for coating. In order to make breaded products, the gel needs to be initially frozen, followed by cutting the gel into desired shapes, as in the case of production of fish sticks or fish fingers. The cut frozen gel shapes (such as sticks) are subjected to coating as described above.

Extrusion cooked products

Extrusion cooking has been employed to manufacture pasta and puffed food products including breakfast cereals, starch-based snack foods and other textured items. The process involves forcing a mixture of starch and other ingredients at a moisture level of 15 - 40% through a barrel under conditions of variable temperature and pressure, when the starch undergoes gelation and binding the other ingredients together in the gel matrix. Movement of the material through the barrel can be effected by single, twin or multiple screw conveyors. Twin or multiple screw extruders have better kneading and mixing properties. High temperature short time (HTST) extruders are gener-

ally used for low moisture foods. The shape of the product can be designed employing suitable dies at the end of the barrel. Extrusion cooking technology has been discussed in detail [41].

Extrusion cooking has been employed for fishery products under defined parameters such as feed composition, feed rate, screw speed, and barrel temperature. A few examples can be cited. Fish snacks were prepared using extrusion temperatures and screw speeds of 95° - 97°C and 220 - 285 rpm, respectively. The products were acceptable, particularly to Asian consumers [42]. A jerky-style snack from salmon meat was developed using twin screw extrusion. The base formulation included Atlantic salmon (82%, w/w), sucrose (4%), pre-gelatinized starch (3%), modified tapioca starch (3%), salt (2%), teriyaki flavoring (2%), and tapioca starch or high-amylose corn starch (4%). The extrusion conditions were: barrel temperature from feed to die, 65o - 155oC; screw speed, 250 rpm; and, feed rate, 220 g/min. The extrudates were subjected to convection-drying at 93°C for 40 min. The process did not adversely affect the nutritional value of salmon meat, particularly its contents of polyunsaturated fatty acids, DHA and EPA. The snack can be appealing to consumers who are interested in the health benefits of fish meat and omega-3 fatty acids [43]. The technology could be applied for production of snacks from shark meat gel. The process, however, needs optimization in terms of extrusion parameters and composition of the feed, of which the shark protein gel is the main ingredient. Preliminary studies have indicated possibility for extrusion cooked shark protein gel products (Venugopal, unpublished data).

Shark meat gel as binder in product development

A number of marine products have shown potential for use as ingredients in bakery and pasta [44]. Shark meat gel, because of its excellent gel strength and stability, can be useful as binder in food products including meat, bakery items, paste, and also fish cutlets, sausages and patties. The binding and emulsifying properties of the gel favor development of low-fat, low-calorie products, having extended shelf life, while the protein content of the product will be comparable with natural meat products. For instance, incorporation of the gel has shown to enhance shelf life of patties prepared from the mince of an underutilized fish [45]. The increasing aquaculture operations demand feeds that are not only nutritious but also stable in pond water for long durations. The shark protein gel has potential as a binder as well as protein source in aqua-feeds to enhance water stability of the feed and hence commercial value.

Other uses

In recent years there has been particular interest for the development of edible coatings from macromolecules such as polysaccharides and proteins to extend shelf life of foods. Such coatings can retain quality of fresh, frozen and processed foods including fish by retarding moisture loss, reducing lipid oxidation and discoloration, enhancing product appearance in retail packages, and also can serve as carriers of food additives such as antimicrobials as well as antioxidant agents [46]. Shark protein gel can be interesting raw material for the development of such edible films intended for fishery products. Dispersions of the gel in water are highly thermostable. Making this property, shark protein powder has been prepared by subjecting the dispersion of the gel to spray drying [47]. Fish sauces are popular items in many countries. Traditionally sauces are prepared by fermenting whole fish for several weeks in presence of salt employing autolytic enzymes present in fish viscera or microbial enzymes [48]. Hygienic and suitably flavored fish sauce has been prepared by fermenting dispersion of the shark meat gel by *Lactobacillus* spp. in presence of small amounts of glucose or lactose at ambient temperature. Fermentation was complete in less than a week and was indicated by fall in initial pH of the dispersion and utilization of sugar by the microorganisms. The fermented sauce had acceptable flavor [49]. The shark protein gel has also good potential for use as fish paneer, a popular Indian product prepared from curdled milk, which is used to prepare curry items. The technology of shark meat gel and its uses for product development can also extended to other Elasmobranchii such as skates and rays, whose meat has similar gel forming characteristics as that of shark.

Conclusion

Shark meat is available in good quantities during fishing operations, particularly as a by-product of fin collection. A novel method for utilization of shark meat is presented. The process makes use of the property of washed shark meat to undergo gelation under mild

acidic conditions. Hardness of the gel is dependent on its moisture content. The gel can be conveniently used for the development of a variety of food products which are valuable protein supplements Although the washing treatment in the process reduces the content of soluble nutrients such as essential amino acids and minerals, the shark protein gel is comparable to the conventional surimi prepared from fish minces. The increasing interests in ready-to-prepare and ready-to-eat products can be the driving force in utilization of shark meat through its gelation properties.

Bibliography

1. Anonymous "Sharks (Chondrichthyes)". VanNostrand's Scientific Encyclopedia (2007).
2. Worm B., *et al*. "Global catches, exploitation rates, and rebuilding options for sharks". *Marine Policy* 40 (2013): 194-204.
3. Dent F and Clarke S. "State of global market for shark products". FAO Fisheries and Aquaculture Technical paper #590, Food and Agriculture Organization, Rome (2015): 197.
4. Vannuccini S. "Shark utilization, marketing and trade". FAO Fisheries Technical paper No. 389. Food and Agriculture Organization, Rome, Italy (1999).
5. Dulvy NK., *et al*. "Challenges and priorities in shark and ray conservation". *Current Biology* 27.11 (2017): R565-R572.
6. Jayasinghe C. "Shark fin cartilage: Uses, extraction and composition analysis". In Marine proteins and peptides: Biological activities and applications (Edited: Se.-Kwon Kim), John Wiley & Sons, Ltd, Chichester, UK (2013).
7. Pomin VH. "Medical gains of chondroitin sulfate upon fucosylation". *Current Medicinal Chemistry* 22.36 (2015): 4166-4176.
8. Venugopal V. "Cosmeceucals from Marine Fish and Shellfish". In Marine Cosmeceuticals Trends and Prospects, (Edited: Se-Kwon Kim) CRC Press, Boca Raton, Fl. USA, (2012) pp.211-232.
9. Venugopal V. "Polyunsaturated fatty acids and their therapeutic functions". In Venugopal, V. Marine Products for Healthcare: Functional and Bioactive Nutraceuticals from the Ocean". Boca Raton, Florida. CRC Press (2009).
10. Jayasinghe C., *et al*. "Inter species changes of lipid compositions in liver of shallow-water sharks from the Indian Ocean". *Fisheries Science* 69.3 (2003): 644-653.
11. Batista L and Nunes ML. "Characterization of shark liver oils". *Fisheries Research* 14:4 (1992): 329-334.
12. Venugopal V., *et al*. "Biochemical characterization of liver oil of Echinorhinus brucus (Bramble Shark) and its cytotoxic evaluation on neuroblastoma cell lines (SHSY-5Y)". *Scientifica (Cairo)* (2016): 6294030.
13. Pastoriza L and Sampredo G. "Loss of urea from the flesh of ray (Raja radiata) during the canning process". *International Journal of Food Science and Technology* 26.2 (1991): 211-213.
14. Venugopal V and Shahidi F. "Structure and composition of fish muscle". *Food Reviews International* 12.2 (1995): 175-197.
15. Økland HM., *et al*. "Proximate composition, fatty acid and lipid class composition of the muscle from deep-sea teleosts and Elasmobranchii". *Comparative Biochemistry. Physiology B Biochemistry Molecular Biology* 140.3 (2005): 437-443.
16. SelfNutrition Data.
17. Ballantyne JS. "Some of the most interesting things we know, and don't know, about the biochemistry and physiology of Elasmobranch fishes (sharks, skates and rays)". *Comparative Biochemistry. Physiology B Biochemistry Molecular Biology* 199 (2016): 21-28.
18. Fraser DI., *et al*. "Widespread occurrence of hydroxyl urea in animals". *PLoS One* 10.11 (2015): e0142890.

19. Mathew S and Shamsundar BA. "Effect of ice storage on the functional properties of proteins from shark (Scoliodon laticaudus) meat". *Nahrung* 46.4 (2002): 220-225.

20. Chanarat S., *et al*. "Non-protein nitrogenous compounds and gelling property of whitecheek shark (Carcharhinus Dussumieri) mince as affected by washing and microbial transglutaminase". *Journal of Texture Studies* 45.4 (2014): 307-316.

21. Méndez A., *et al*. "Production, characterization and application of protein isolates from shark. Part 3. Characterization of protein isolates". *Nahrung* 26.6 (1982): 533-540.

22. Diniz FM and Martin AM. "Optimization of nitrogen recovery in the enzymatic hydrolysis of dogfish (Squalus acanthias) protein. Composition of the hydrolysates". *International Journal of Food Science and Nutrition* 48.3 (1997): 191-200.

23. Sun X-D and Holley RA. "Factors influencing gel formation by myofibrillar proteins in muscle foods". *Comprehensive Reviews in Food Science and Food Safety* 10.1 (2011): 33-51.

24. Park JW. "Surimi and Surimi Seafood". CRC Press, Boca Raton, Fl (2014): 637.

25. Oakenfull D., *et al*. "Protein gelation". In Food proteins and their applications. S Damodaran, S and Paraf A, Editors, Marcel Dekker, New York (1997): 111-131.

26. Niwa E. "Chemistry of surimi gelation". In Surimi Technology, Lanier, TC and Lee, CM. Eds., Marcel Dekker, New York (1992): 389-395.

27. Totosaus A., *et al*. "A review of physical and chemical protein gel induction". *International Journal of Food Science and Technology* 37:6 (2002): 589-601.

28. Stone AP and Stanley DW. "Gelation of fish muscle proteins". *Food Research International* 25.5 (1992): 381-388.

29. Martin-Sanchez AM., *et al*. "Alternatives for efficient and sustainable production of surimi". *Comprehensive Reviews in Food Science and Food Safety* 8.4 (2009): 359-374.

30. Kailasapathy K and Salampessy J. "Suitability of shark flesh for surimi production". *Food Australia* 51.3 (1999): 110-115.

31. Fretheim K., *et al*. "Slow lowering of pH induces gel formation of myosin". *Food Chemistry* 18.3 (1985): 169-178.

32. Venugopal V., *et al*. "Gelation of shark myofibrillar proteins by weak organic acids". *Food Chemistry* 50.2 (1994): 185-190.

33. Kakatkar A., *et al*. "Hydration of muscle proteins of Bombay duck (Harpodon nehereus) during acetic acid-induced gelation and characteristics of the gel dispersion". *Food Chemistry* 83.1 (2003): 99-106.

34. Karthikeyan M., *et al*. "Effect of water washing on the functional and rheological properties of proteins from threadfin bream (Nemipterusjaponicus) meat". *International Journal of Food Science and Technology* 41.9 (2006): 1002-1010.

35. Venugopal V., *et al*. "Gelation of shark meat under mild acidic conditions: Physico-chemical and rheological characterization of the gel". *Journal of Food Science* 67.7 (2002): 2681-2686.

36. Pearson AM and Tauber FW. "Restructured meat products". In Processed Meat, Springer, Netherlands (1984): 329-350.

37. Venugopal V., *et al*. "Restructured shelf stable steaks from shark meat gel". *Food Science and Technology LWT* 35.2 (2002): 185-189.

38. Flick GJ., *et al*. "Processing finfish". In The Seafood Industry, Martin RE and Flick GJ, Editors (1990): 117-122.

39. Fiszman SM and Salvador A. "Recent developments in coating batters". *Trends in Food Science and Technology* 14.10 (2003): 399-407.

40. Venugopal V. "Coated products". In Seafood processing: Adding value through quick freezing, retortable packaging and cook-chilling, CRC Press.

41. Guy R. "Extrusion cooking: Technologies and applications". Woodhead Publ. Abington, Cambridge (2001): 201.

42. Suknark K., *et al*. "Acceptance by American and Asian consumers of extruded fish and peanut snack products". *Journal of Food Science* 63.4 (1998): 721-725.

43. Kong K., *et al*. "Composition and consumer acceptability of a novel extrusion-cooked salmon snack". *Journal of Food Science* 73.3 (2008): S118-S123.

44. Kadam SV and Prabhasankar P. "Marine foods as ingredients in bakery and pasta products". *Food Research International* 43.8 (2010): 1975-1980.

45. Smruti K., *et al*. "Shelf life enhancement of hardhead catfish (Arisfelis) patties making use of acetic acid induced gelation of the fish proteins". *Fishery Technology (India)* 41.2 (2004): 121-124.

46. Cuq B., *et al*. "Edible packaging films based on fish myofibrillar proteins: Formulations and functional properties". *Journal Food Science* 60.6 (1995): 1369-1373.

47. Venugopal V., *et al*. "Thermostable water dispersions of shark meat and its application to prepare protein powder". *Journal of Aquatic Food Product Technology* 6.3 (1997): 53-67.

48. Owens JD and Mendoza LS. "Enzymatically hydrolysed and bacterially fermented fishery products". *Journal of Food Technology* 20.3 (1985): 273-278.

49. Sree Rekha PS., *et al*. "A process for convenient production of hygienic fish sauce by lactic acid fermentation of shark meat gel". *Fishery Technology (India)* 39.2 (1989): 124-129.

Volume 10 Issue 3 August 2017