CHAPTER II

Literature Review

This chapter briefly describes protein gel development, especially surimi gel, and the deep-fat frying process. First, it introduces the details of surimi gelation including the raw materials and its components which affect the quality of the gel, and then presents the microstructural studies in the field. Thereafter, it describes the frying process and presents some fried food characteristics. Subsequently, this chapter reviews researches in the field that have been undertaken to understand heat and mass transfer mechanisms. Finally, it focuses on oil absorption kinetics research and introduces the main factors affecting oil absorption.

2.1 Proteins

2.1.1 Protein Structure

Proteins are highly complex polymers, made up of 20 different amino acids (Fennema, 1996). They are not linear molecules but have an intricate three-dimensional structure that is unique to each protein. It is this three-dimensional structure that allows proteins to function. Thus in order to understand the details of protein function, one must understand protein structure (Gorga, 1999).

Four levels of protein structure including primary structure, secondary structure, tertiary structure and quaternary structure can be distinguished:

2.1.1.1 Primary Structure

Primary structure refers to the linear sequence of amino acids. The primary structure is sometimes called the covalent structure of proteins because, with the

exception of disulfide bonds, all of the covalent bonding within proteins defines the primary structure. In contrast, the higher orders of protein structures (i.e. secondary, tertiary and quaternary) involve mainly non-covalent interactions (Gorga, 1999).

2.1.1.2 Secondary Structure

Secondary structure is the locally ordered structure brought about via hydrogen bonding mainly within the peptide backbone. The most common secondary structure elements in proteins are the alpha (α) helix and the beta (β) sheet (Gorga, 1999).

The α-helix contains 3.6 amino acid residues per turn. Each peptide can be considered as a plane that is tangent to the axis of the helix. There are 100 degrees of rotation from one amino acid to the next. Each peptide group is hydrogen bonded to the third peptide along the chain in either direction. This is a very compact structure that does not have room for water or other small molecules in the interior (Mangino and Litchfiled, 2004).

The β-sheet structure is an extended structure with specific geometries. In this extended form, the C=O and N-H groups are oriented perpendicular to the direction of the chain, and therefore hydrogen bonding is possible only between segments, and not within a segment. The β-strands are usually about 5-15 amino acid residues long. In proteins, two β-strands of the same molecule interact via hydrogen bonds, forming a sheet-like structure known as a β-pleated sheet. In the sheet-like structure, the side chains are oriented perpendicular to the plane of the sheet. Depending on the N→C directional orientations of the strands, two types of β-pleated sheet structures, namely parallel β-sheet and antiparallel β-sheets, can form. Antiparallel β-sheets in general are more stable than parallel β-sheets (Fennema, 1996).

2.1.1.3 Tertiary Structure

Tertiary structure is the global folding of a single polypeptide chain. A major driving force in determining the tertiary structure of globular proteins is the hydrophobic effect. In a polar solvent the polypeptide chain folds such that the side chains of the nonpolar amino acids are hidden within the structure and the side chains of the polar residues are exposed on the outer surface. Hydrogen bonding involving groups from both the peptide backbone and the side chains is important in stabilizing tertiary structure. The tertiary structure of some proteins is stabilized by disulfide bonds between cysteine residues (Gorga, 1999).

2.1.1.4 Quaternary Structure

The quaternary structure involves the association of two or more polypeptide chains into a multi-subunit structure. Quaternary structure is the stable association of multiple polypeptide chains resulting in an active unit. Not all proteins exhibit quaternary structure. Usually, each polypeptide within a multi-subunit protein folds more or less independently into a stable tertiary structure and the folded subunits then associate with each other to form the final structure.

Quaternary structures are stabilized mainly by non-covalent interactions. All types of non-covalent interactions: hydrogen bonding, van der waals interactions and ionic bonding, are involved in the interactions between subunits. In rare instances, disulfide bonds between cysteine residues in different polypeptide chains are involved in stabilizing quaternary structure (Fennema, 1996; Gorga, 1999).

2.2 Protein Gel

Protein gels are formed when partially unfolded proteins develop uncoiled polypeptide segments that interact at specific points to form a three dimensional cross-linked network. The partial unfolding of proteins with slight changes in secondary structure is required for gelation. Schmidt (1981) defined gelation as a

protein aggregation phenomenon in which polymer-polymer and polymer-solvent interactions are so balanced that a tertiary network or matrix is formed.

Gel formation is a result of hydrogen bonding, ionic and hydrophobic interactions, Van der Waals forces, and covalent disulfide bonding. Cross-links are the determining factor in the formation of the rubbery nature of protein gels. Decreasing the number of cross-links should decrease gel hardness. A unique property of protein gels is that they behave as a solid-like material, but, at the same time, they possess many characteristics of a fluid. The gelation phenomenon is responsible for the solid-like, viscoelastic properties of foods, increased viscosity, adhesiveness and improved water retention. These specific properties of gels are due to the presence of a three-dimensional network (Zayas, 1997).

Surimi is a concentrate mass of the myofibrillar proteins of fish muscle that is mechanically deboned and water-washed. Since the early 1980s, sales of surimi-based products have rapidly grown, and surimi gel, which is essentially a protein gel, is a key product. This gel is manufactured by grinding raw or frozen surimi with salt and other ingredients, followed by extrusion, fiberized, or composite-moulding depending upon the product desired and finally heated to set the shape, develop the texture, and pasteurize the product (Lanier and Lee, 1992).

2.3 Fish as Raw Material

2.3.1 Threadfin Bream

The threadfin bream (*Nemipterus* spp.) belong to the family Nemipteridae, and about 10 species are commonly found in the Indo-West Pacific region in tropical and subtropical waters. Catches of threadfin bream are usually not identified by species, but in the Southeast Asian region the main species caught include *Nemipterus peronii*, *N. marginatus*, *N. mesoprion*, *N. nematophorus*, and *N.japonicus*. Most of these species are 12-25 cm long, but the common size for the smallest species. *N. rnesoprion*, is about 10 cm. This species

is usually landed as by-catch. The larger sized fish are usually sorted out for sale as whole fish for direct consumption.

Threadfin bream forms an important part of the trawl catch, with the greatest catches being landed in Thailand, Indonesia, the Philippines, and Malaysia. The fish are benthic, inhabit marine waters on sandy or muddy bottoms usually in depths of 20-50 m, and feed on small benthic invertebrates and small fish. Males are usually larger, and some species may be protogynous hermaphrodites. Two prolonged spawning seasons occur from November to February and another from May to June.

This threadfin bream surimi is now well accepted in Japan. Because of the white color, smooth texture, and strong gel-forming ability of the fish meat, threadfin bream is also widely used as raw material for Japanese "kamaboko" and surimi crabsticks (Park, 2000).

2.3.2 Cod

The cod (*Gadus morhua*) belong to the family Gadidae. It is probably the best-known fish caught commercially in UK waters. In appearance, the head is rather disproportionately large for the body, with the upper jaw protruding over the lower. The colour of the body can vary depending on the habitat in which the fish is found, but ranges from reddish or greenish where the water is populated by algae, and pale grey where the fish is found in deep water or near a sandy bottom. The cod has a barbell on the end of its chin and, in common with several other members of the family, three dorsal and two anal fins. The tail fluke is square-ended, and the lateral line is noticeable and extends from the point of the gill covers to the center of the tail root (Anonymous, 2004).

The Atlantic cod is commonly found in North Atlantic from Cape Hatteras to Ungava Bay along the North American coast, east and west coast of Greenland, around Iceland, coasts of Europe from the Bay of Biscay to the Barents Sea,

including the region around Bear Island. This species is widely distributed in a variety of habitats, from the shoreline down to the continental shelf. Cod form schools during the day. Cod are omnivorous; they feed at dawn or dusk on algae, invertebrates and fish, including young cod. Cod spawn once a year. They are marketed fresh, dried or salted, smoked and frozen; they are eaten steamed, fried, broiled, boiled, microwaved and baked. The most important stocks are the Norwegian Arctic stock in the Barents Sea and the Icelandic stock. The populations around Greenland and Newfoundland have declined dramatically (Cohen et al., 1990).

2.4 Protein Components of Surimi

Fish muscle consists of two main types, white (or light) and red (or dark), depending on the life-cycle of the species concerned. Strong swimming species, such as tuna and mackerel have a larger proportion of dark muscle than relatively sluggish fish such as cod, haddock and flat fish. White muscle is mainly composed of proteins and amounts to 65 to 75% of the total mass. The red muscle varies from 1 to 2% and is found as a "V" shaped stripe beneath the lateral line and also in other areas such as the dorsal region (Stanby, 1982; Hall and Ahmad, 1997). Red muscle contains more mitochondria and less sarcoplasmic reticulum than white muscle. Red muscle also has higher lipid (2-5 times), heme pigments such as myoglobin, B vitamins, glycogen, nucleic acid and carbohydrate (glycogen) contents when comparing to white muscle. Furthermore, red fibres contain higher concentrations of the enzymes involved in the tricarboxylic acid cycle, electron transport. glycogen synthesis and lipolysis, while white fibres contain greater contents of ATPase activity, glycolytic acids and water (Sikorski et al., 1990), The red muscle is designed for long-term exercise and is used by migrating species that travel great distances, while the white muscle is believed to function when bursts of speed of short duration are needed.

The amount of protein in fish flesh ranges from 15% to 19% of which 20% - 30% are sarcoplasmic protein (myoglobin, haemoglobin, etc.); 70%-80% are

structural proteins (myosin, actin, tropomyosin, etc.); and 2% to 3% are connective tissue (mainly collagen) proteins (Venugopal and Shahidi, 1996; Park, 2000).

2.4.1 Myofibrillar Proteins

Myofibrillar proteins, primarily myosin and actin (F and G types), constitute the contracting structure of the muscle fibers and contribute most to the formation of heat-induced gels. The myosin molecule is composed of two heavy chains (200 and 240 KD) associated non- covalently with two pairs of light chains, essential light chain and regulatory light chain, to form the globular head (Venugopal and Shahidi, 1996). The essential light chains are also known as alkaline light chain, LC-1 (20.7-25 KD) and LC-3 (16-16.5 KD), as they are dissociated from myosin only at high pH. The regulatory light chains are also called DTNB light chains or LC-2 (19-20 KD) as they are removed from myosin by treatment with 5,5' dithiobis (2-nitrobenzoic acid) (DTNB) (Asghar et al., 1985). The long myosin rod can be split by trypsin into two fragments called light meromyosin (LMM) and heavy meromyosin (HMM). LMM is soluble in water, but is soluble at ionic strengths above 0.3, has neither ATPase activity nor actin-binding ability, is almost 100% α-helical and under certain conditions will form filaments that resemble thick filaments. HMM is soluble in water, has both ATPase activity and actin-binding ability, does not form filaments, is approximately 45% α-helical and consists of two globular heads attached to a short rod. HMM can be cleaved into two different fragments, subfragment 1 (HMM-S1) and subfracment 2 (HMM-S2). One mole of myosin consists of two moles of HMM-S1 and one mole of HMM-S2 (Goll et at., 1977).

Fish myosin is more sensitive to denaturation, coagulation, degradation and chemical changes than mammalian myosin. However, myosin stability varies among fish species. Tropical fish myosins such as those from snapper (*Lutianus sebae*), cat fish (*Clarious gariepinus*), carp (*Cyprinus carpio*) are

more stable than those from cold-water fish such as cod (*Gadus morhua*) and trout (*Salmo gairdnevi*).

Actin contains only one polypeptide chain. One molecule of actin contains one molecule of ATP and one molecule of Ca^{2+} (Mg^{2+} can be substituted for the Ca^{2+}). The actin can, under certain conditions including monovalent salt concentrations of 50-500 mM or Mg^{2+} or Ca^{2+} concentrations above 1 mM, aggregate to form a double-stranded helical filament. G actin polymerizes to form the filamentous F actin in the presence of neutral salt (Poulter et al., 1985; Davies et al., 1988; Howell et al., 1991; Angsupanich, 1998; Park, 2000).

Myofibrillar proteins are soluble in mild salt (NaCl) solution (1-8%), but are largely insoluble in water of lower ionic strength (~0.05-~0.5%). The solubility of myofibrillar proteins is, however, enhanced when the ionic strength approaches zero. In preparing the meat for gel formation by cooking, salt is added to enhance solubility and thus aid dispersion of the proteins. The increasing solubility of myofibrillar proteins near zero ionic strength can possibly contribute to their loss during surimi manufacture should the washing step be too extensive (Park, 2000).

2.4.2 Stroma Proteins

Connective tissue (stroma) proteins consist of ground substance, elastin and collagen which is the major protein of these tissue. These proteins are almost totally insoluble in water or saline and do not participate in gel formation. Because the basis of the conventional surimi manufacturing process is the leaching out of water soluble components, collagen is retained along with the myofibrillar proteins when surimi is made. Collagen can convert to gelatin when heated, depending on the structure of the collagen present. This soluble gelatin can interfere with the gelation of the myofibrillar proteins and/or accumulates in unsightly pockets in the product. However, fish have only a small percentage of stroma proteins relative to the myofibrillar protein content and, therefore, the presence of collagen has a negligible effect on the gelling ability of surimi. Unfortunately, the opposite is true for mammalian and avian species. Unless a new processing step is introduced to reduce connective tissue content, surimi prepared from these species can be negatively affected (Park, 2000).

2.4.3 Sarcoplasmic Proteins

Sarcoplasmic proteins are the components of extra-cellular fluid, they are usually of low molecular weight and are the most soluble. Included in sarcoplasmic proteins are myoglobin, haemoglobin, globulins, albumins, lysosomes, peptides and various enzymes (Venugopal and Shahidi, 1996; Angsupanich, 1998).

Most sarcoplasmic proteins, in contrast to the fibrillar or rodlike conformation of myosin and actomyosin, are globular (round) in tertiary structure. Being water soluble, sarcoplasmic proteins are largely removed by the conventional leaching process in surimi manufacture. Sarcoplasmic proteins, if not removed, would dilute the concentration of the better gelling myofibrillar proteins and adversely affect surimi gelation. If sarcoplasmic proteins are present when the myofibrillar proteins are heated during food manufacture, they

may denature and attach to the myofibrillar proteins, also decreasing the gelling ability of surimi (Park, 2000).

2.5 Endogenous Enzymes in Surimi

Temperature plays an important role in surimi gelation. In addition to its effects on the conformation of myofibrillar proteins, temperature can activate endogenous enzymes that naturally occur in fish muscle. Fish muscles from various species show similar reactions to temperature: a structure-setting reaction below 40°C (low temperature setting), and a structure-disintegration reaction at 50-70°C (known as modori). Low-temperature setting is associated with transglutaminase activity, whereas modori is induced by endogenous thermostable proteinases that can degrade myosin rapidly (An et al., 1996).

2.5.1 Endogenous Transglutaminase (TGase)

The increase in the gel strength of surimi in low-temperature setting (4-40°C) is associated with TGase activity. Endogenous TGase is water soluble and can be removed if washing is too extensive. TGase catalyzes acyl-transfer reactions in which the γ-carboxamide group of peptide-bound glutamine serves as the acyl donor. When the ε-amino group of peptide-bound lysine acts as the acceptor, the ε-(γ-glutamyl) lysine bond is formed between the proteins, resulting in their crosslinking.

High variability in the TGase activity of surimi is common and is due to a combination of factors. First, TGase is a water-soluble enzyme and thus its content can vary greatly with the type and extent of purification process used during surimi manufacture. Second, it is likely that different fish species, and perhaps different individuals within species, could vary in natural content of the enzyme, possibly affected by habitat, feed, and physiological condition. This possibility has not been well investigated to date. A third possible contributing factor is that the α_2- macroglobulin component of fish blood

plasma (or added beef plasma) has the ability to form ε-(γ-glutamyl) lysine cross-links in fish protein. Last, it has been shown that in certain species, such as salmon, the water-soluble fraction of muscle also contains factors that inhibit TGase activity (An et al., 1996; Park, 2000).

2.5.2 Proteolytic Enzymes

Most fishes also possess heat-stable proteolytic (protein-degrading) enzymes (proteases). The source, type, and content of proteases can vary greatly for each species. Such enzymes disintegrate the protein network being formed by the gelation of the myofibrillar proteins, resulting in a mushy, rather than firm, gel texture. These proteases attack the muscle proteins most actively during the cooking of the surimi seafood, when the temperature is between 50-70 °C. Some of these heat-stable proteases (in croakers, tilapia, and some pelagic fish) are most active at higher pH (alkaline or neutral proteases, most active near pH 8.0), whereas others, such as those in Pacific whiting, are most active at pH 5.5 (cathepsin L). However, all are still quite active over the pH range of most surimi and minced fish, which lies between 6.0 and 7.5.

Proteolytic enzyme(s) are inactivated by heating at 80°C or greater; therefore rapid cooking, such as ohmic or microwave heating, eliminates the problem. In addition, blood plasma protein and some other naturally derived proteins. such as those from egg, potato, and whey, when added to surimi inhibit the degradative activity of the enzymes. These are the primary means of enzyme control in surimi made from parasitized Pacific whiting and perhaps a safe precaution when using surimi or mince of any species (Park, 2000).

2.6 Gelation Mechanism

Gels behave as solid-like materials, but, at the same time, they possess many characteristics of fluids. Gels consist of polymeric molecules, or submicroscopic particles, cross-linked to form an intermolecular network immersed in a liquid medium. In food gels, the molecular network consists of proteins or polysaccharides or a combination of the two and the liquid is water. The polymer molecules form a three-dimensional network and the complex interaction between the solvent and molecular network prevents water from flowing away. In rheological terms, a gel is a viscoelastic material as it has both solid and liquid rheological properties (Oakenfull et al., 1997). In order to study a viscoelastic material, dynamic measurements in which an oscillatory strain or stress is acted on the sample and the response to this oscillatory stress or strain, is measured. Two independent parameters are obtained from dynamic measurements: the storage modulus (G') describes the amount of energy that is stored elastically in the structure and the loss modulus (G") is a measure of the energy loss or the viscous response (Hermansson, 1994). For a gel, G' is greater than G" and both G' and G" are almost independent of frequency (Oakenfull et al., 1997).

Thermal gelation of fish muscle proteins occurs in three-steps including (1) dissociation of myofibril structures by protein solubilisation in the presence of salt (2) denaturation of the proteins with concomitant conformational changes caused by heat treatment (3) aggregation of unfolded protein via hydrogen and disulphide bonds, electrostatic and hydrophobic interactions, to form a three-dimensional structure (Stone and Stanley, 1992).

The mechanism for protein gelation suggested by Ferry (1948) is as follows:

$$XP_N \Rightarrow XP_D \Rightarrow (P_D)_X$$

where X is the number of protein molecules, P_N is the native protein and P_D is the denatured protein. According to the Ferry theory, the final gel state corresponds to aggregates of partly denatured protein. Thus, when proteins are denatured, they link together to build the networks (Ferry, 1948).

2.7 Surimi Gel Formation

The formation of a fish gel as a function of temperature involves 3 steps, suwari (setting), modori (network softening) and kamaboko (gel strengthening). The first stage "setting" occurs when fish mince sol (paste) is heated to 50 °C, a loose network is formed from actomyosin and myosin. Hydrophobic interactions between the heavy meromyosin S-2 (HMM S-2) and light meromyosin (LMM) of the myosin tail contribute to this formation (Stone and Stanley, 1992). The α-helix unfolding increases the surface hydrophobicity, promoting these interactions. Ishioroshi et al. (1979) indicated that at temperatures as low as 35 °C the fusion of the head portion of myosin molecules may occur. The unfolding of the helical tail portion of the myosin molecule by heat then leads to the heat-induced gelation of myosin. Other forms of interaction, such as hydrogen bonding, disulphide bonding, electrostatic interactions and enzyme catalysed cross-links may also be present. The second stage, modori, takes place around the incubation temperature near 60 °C which favours alkaline protease activity, resulting in a decrease in gel rigidity. The last stage, kamaboko is when further heating above 60-70 °C leads to increased gel strength due to further aggregation of myosin head regions (HMM S-1) and further oxidation of sulfhydryl group and subsequent disulphide bond formation which helps strengthen the gel (Niwa, 1992).

Setting at low temperature prior to heating at a higher temperature allows slow ordering of the protein molecules resulting in good gelation (Lanier et al., 1982). This agrees well with the suggestion of Hermansson (1978) that the denaturation of protein prior to aggregation results in a finer structure with greater elasticity than found from random aggregation occurring simultaneously or prior to denaturation.

However, a different gel structure results when the gel is prepared by direct heating at high temperatures without first undergoing setting. Rapid unfolding of the proteins results in more intense coagulation, thereby more water is released from the gel and the protein dispersion becomes very uneven. The resulting gel is quite white, opaque, compact and exhibits less uniform structure, lower elasticity and water-binding capacity, than gels prepared after an initial setting step (Niwa, 1992).

2.8 Microstructure of Protein Gel

Many proteins have the ability to form different types of network structure depending on factors such as temperature, pH, and the presence of salts. Such gels can be divided roughly into fine-stranded and coarse aggregate gels. Fine-stranded gels are formed by an ordered association of molecules, and the dimensions are often so small that these gels are transparent. On the contrary, aggregate gels, such as surimi gels (kamaboko), are non-transparent (Hermansson, 1994).

The structural characteristics of the matrix and the type of intermolecular interactions occurring under different processing conditions determine the functional properties and texture of gels. In heat-induced gels, the protein must denature and aggregate to form the network. After heating, a complex protein like myosin may undergo multiple conformational changes attributable to the different thermal stabilities of the various structural domains or protein subunits (Smyth et al., 1996) The endothermic temperature-induced changes may involve dissociation of non-covalent bonds in a particular structural domain or dissociation of myofilaments or protein subunits (Lesiow and Xiong, 2001).

The degree of necessary unfolding of protein into uncoiled polypeptides to initiate aggregation depends on the ionic environment, thermal processing conditions, and intrinsic factors of the proteins (conformation, isoforms, etc). These factors play essential roles in developing gel structure and maintaining its rigidity or strength and resistance to external forces. It is suggested that the unfolding step

should occur first and more quickly than aggregation to allow the denatured protein molecules to re-orient themselves, interact at specific points, and finally form an ordered three-dimentional network structure (Ziegler and Acton, 1984; Foegeding, 1988; Lin and Park, 1996; Alvarez et al., 1999).

Alvarez et al. (1999) studied, by scanning electron microscopy (SEM), the microstructure of suwari and kamaboko gels made from sardine surimi, where the only variables were the heat setting conditions, which had shown differences in texture. They found that the various setting time-temperature combinations had an effect on suwari and kamaboko networks and gave rise to differences in texture. The results suggested that the final structure of kamaboko networks was the outcome of denaturation-aggregation during setting of the surimi sol, and that this determined the possibility of reorganisation of the molecules to form the final network.

The strength and properties of the gel depend on the nature of the network including its porosity, size, the included gas and liquid phases. Thinakorn (1998) studied the factors affecting the structures and properties of high density polyethylene (HDPE)/ natural rubber (NR) foam. She found that increasing the gas phase fraction resulted in a decrease in hardness and tensile strength. Similarly Hug (2001) reported that the compression force depended on the foam cell geometry characterised by the cell size, normally expressed as pores per inch. It has a rather similar air bubble distribution as in kamaboko gel structure. Thus, it is evident that there is a significant relationship between the structure and the strength of the gel.

2.9 Deep-Fat Frying

Generally, deep-fat frying is defined as a process for the cooking of foods by immersing them in an edible fluid (fat), at a temperature above the boiling point of water (Farkas, 1994). Frying temperatures can range from 130 to 190°C, but the most common temperatures are 170 to 190°C. This process involves simultaneous heat and mass transfer resulting in counterflow of vapor and oil at the surface of the piece (Bouchon, 2002).

Frying creates unique texture and flavors in foods. As a result, fried foods exhibit a dry, porous, crisp and oily outer layer (or "crust"), and a moist cooked interior (or "core") whose microstructures have been formed during the frying process. Crust formation is the result of changes in the original structure of the raw material after exposure to hot oil, namely; in the case of starchy, proteinaceous foods, softening of the middle lamella between cells, starch gelatinization inside the cells, protein denaturation, water evaporation and rapid dehydration of the tissue, and finally, oil uptake (Pedreschi et al., 2001).

2.10 Fried Products

Consumption of a wide variety of fast foods including convenience and snack foods continues to increase in all countries. Many of these foods, including french fried potatoes, chicken and fish pieces, potato crisps, corn chips, tortilla chips, extruded snacks and doughnuts are prepared by deep-fat frying (Smith et al., 1985). Fried products can be classified according to their surface-to-volume ratios, i.e., products that have: (1) large interior (crumb) volume and no crust differentiation, such as chicken meat below the breading crust; (2) large interior volume and large surface area, with a crust differentiating the surface from the crumb, such as french fries; and (3) small interior volume, large surface area, and all crust (no crumb) as in the case of potato crisps (Blumenthal, 1991; Moreira, et al., 1999).

One of the most important quality parameters of those products is the amount of fat absorbed during the frying process. Excess consumption of fat is considered as the key dietary contributor to coronary heart disease and perhaps cancer of the breast, colon, and prostate. Also, some compounds developed during the prolonged use of fat for deep-fat frying are of questionable desirability. The possibility exists that a few toxic breakdown products may be mutagenic (Saguy and Pinthus, 1995). These are the main reasons for the need to reduce oil uptake during frying. Hence, a knowledge of the structure, composition, and properties of food products is useful in understanding their frying characteristics. The product structure may affect oil content; for example, french fries have about 30-50% less oil content per unit mass than potato crisps. The product composition influences the oil absorption and structure characteristics; for instance, low-moisture tortilla dough results in tortilla chips with lower oil content and larger pore size distribution. The physical properties of the product control the rate of temperature increase; an example is the effect of crust thickness that will cause a barrier for heat transfer from the surface to the center of the product (Moreira et al., 1999).

2.11 Heat and Mass Transfer during Deep-Fat Frying

Deep-fat frying is a thermal process involving simultaneous heat and mass transfer. Heat transfer during frying can be distinguished into two modes — convection and conduction. Convective heat is transferred from the oil to the surface of the product and, thereafter conductive heat transfer predominantly occurs inside the food. Mass transfer is characterized by the loss of water vapor from the food and the movement of oil into the food (Singh, 1995).

Farkas (1994) developed a predictive heat transfer model. He observed that the temperatures in the core region are restricted to values below the boiling point of the liquid in the product which is slightly higher than the boiling point of water due to the presence of solutes. As the frying process proceeds, more water evaporates from the outer regions of food. Consequently, the temperature of the dried regions

(i.e. in the crust) begins to rise above the boiling point. On the basis of visual observations, Farkas suggested that the frying process is composed of four distinct stages:

1) Initial heating, which lasts a few seconds, the surface of a food submerged in oil heats to a temperature equivalent to the elevated boiling point of liquid. The mode of heat transfer between the oil and the food is due to natural convection, and no vaporization of water occurs from the surface of the food.
2) Surface boiling, which is characterized by the vaporization process, the beginning of the crust formation and forced convection due to the presence of considerable turbulence in the oil surrounding the food.
3) Falling rate, which is the longest, in which the internal moisture leaves the food, the internal core temperature rises to the boiling point, the crust layer increases in thickness, and finally the vapor transfer at the surface decreases.
4) End of Bubbling, which is the final stage of moisture loss and bubbles escape (frying is usually stopped before this point).

The convective heat transfer coefficient is defined as the rate of interfacial heat transfer convected through unit surface area of the material when a unit temperature gradient exists between the product surface and the surrounding fluid. It is important in modeling and design of frying systems. Several authors have attempted to measure natural convective heat transfer coefficients, typically using a metal transducer. Miller et al. (1994) measured the heat transfer coefficients of canola, soybean, and palm oils at temperatures ranging from 170 to 190°C. A spherical aluminium transducer was used to determine the convective heat transfer coefficient. Values for the heat transfer coefficient ranged from 251 to 276 Wm^{-2} $°C^{-1}$. Palm oil was the most affected by temperature. Tseng et al. (1996), using a copper sphere, found the convective heat transfer coefficient to be 279 Wm^{-2} $°C^{-1}$ for soybean oil heated at 190°C. Bouchon (2002), using the lumped capacity method, found the natural convective heat transfer coefficient to be 262 to 282 Wm^{-2} $°C^{-1}$ for palm olein oil heated from 155 to 185 °C. These values are in agreement with those reported by both Miller et al. (1994) and Tseng et al. (1996).

2.12 Kinetics of Oil Uptake

The kinetics of oil uptake is crucial to reveal how and when the oil penetrates inside the structure. Ufheil and Escher (1996) studied the dynamics of oil uptake during deep-fat frying of potato slices by frying the slices for an equal length of time, but introducing a fat-soluble and heat stable dye into the oil (Sudan Red B) at different times before the end of frying and measuring the fraction of dyed oil present in the slices in relation to the total oil content. They found that, even when the dyed oil was added a few seconds before the slices were removed from the frying pan, the fraction of non-dyed oil was minimum. As a result, they suggested that oil uptake is primarily a surface phenomenon, involving an equilibrium between adhesion and drainage of oil upon retrieval of the slice from the oil.

In an additional study on tortilla chips, Moreira et al. (1997) found that the highest proportion of oil penetrates into the structure during the post-frying cooling period. Their results showed that only 20% of the total oil content was absorbed during frying, and of the remaining oil, 64% was absorbed during cooling and 36% was left on the surface. In a further study, Moreira and Barrufet (1998) explained the mechanism of oil absorption during cooling in terms of capillary forces. Their model suggested that, during frying, the transfer of heat to the sample was controlled by convection and conduction; during cooling, the surface oil and the surrounding gas was controlled by capillary pressure. The average mass of gas within the pore increases during frying and cooling. The pore size, on the other hand, increases during frying, but remains constant during cooling when both gas and oil compete to fill the void spaces. The bulk volume of the tortilla chips and the water content are constant during cooling. The results showed higher oil content for tortilla chips with higher initial moisture content, smaller radius, lower cooling air temperature and higher interfacial tension between oil and gas.

Models for oil absorption should not only consider the oil that is absorbed during the cooling period, but also the draining phenomenon occurring on the surface of the product. Bouchon et al. (2003) analysed the oil absorption process in

deep-fat fried potato cylinders at frying temperature of 155, 170 and 185 °C. The oil penetrated was distinguished into three fractions: structural oil (absorbed during frying), penetrated surface oil (suctioned during cooling), and surface oil. They found that a small amount of oil penetrated during frying, whereas most of the oil was picked up at the end of the process, corresponding mainly to a surface phenomenon occurring when the sample is removed from the oil. After cooling, the oil was found to be located either on the surface of the chip or suctioned into the porous crust microstructure. Further, they reported an inverse relationship between the surface oil and suctioned oil for increasing frying times. They suggested that (1) the largest proportion of the oil, which ends up in the fried potato, is sucked into the porous crust region after the potato is removed from the oil. And (2) the balance between oil in the crust and residual surface oil is the result of the competition between capillary suction into the crust region and drainage along the surface of the product.

Pinthus and Saguy (1994) described the relationship between the initial interfacial tension between a restructured potato product and frying medium, and the medium-uptake during deep-fat frying, by using a fundamental approach based on surface chemistry. They found that the total oil uptake was higher for lower initial interfacial tensions due to the increased wetting adhesion, reflecting the importance of wetting phenomena.

It is evident that the physical and chemical properties of the frying media are extremely relevant to the oil uptake mechanisms. Tseng et al. (1996) evaluated the effect of oil degradation on the thermal and physical properties of soybean oil and determined how the quality attributes of tortilla chips were affected by oil degradation. They found that the total oil content and fracturability of tortilla chips were not affected significantly by oil degradation. However, the oil content adhering to the surface of the chips was significantly higher when the chips were fried in degraded oil than in fresh oil. After allowing the chips to cool down, only 19% of the

total oil content was on the surface of the chips fried in fresh oil, while 49% remained at the surface of the chips fried in the degraded oil.

2.13 Factors Affecting Oil Uptake

A wide range of factors have been reported to affect oil uptake. The main factors are discussed below.

2.13.1 Oil Quality and Composition

The influence of oil quality and composition on uptake is widely documented. As mentioned above in secton 2.6, Pinthus and Saguy (1994) showed that an increase in the initial interfacial tension between oil and restructured potato products, decreased oil absorption. Further, oil degradation also produces surfactants, which act as wetting agents promoting the absorption (Blumenthal, 1991).

2.13.2 Frying Temperature

Gamble et al. (1987) found no correlation between oil temperature and oil content when frying potato slices, but concluded that a lower oil temperature resulted in a lower oil content in the early stages of frying with a greater difference between 145 °C and 165 °C than between 165 °C and 185 °C. Similarly, Moreira et al. (1997) determined higher differences in oil absorption between 130 °C and 160 °C than between 160 °C and 190 °C. In addition, Moreira et al. (1995) determined that the oil absorption rate was unaffected by the oil temperature when frying tortilla crisps and that a frying temperature of 190 °C gave a higher oil content (3% to 5%) than a frying temperature of 155 °C.

2.13.3 Product Shape

The geometrical shape, that is, the ratio of surface area of the product to its volume (i.e. specific surface area) plays an important role in oil penetration. For example, french fried potatoes contain only 13.5% oil on average, whereas the fried potato crisp contains about 40% oil, because the specific surface area of potato crisp is 10 to 15 times greater than that of the french fried potato. Bouchon and Pyle (2004) found that oil absorption decreased significantly when increasing the thickness of restructured potato chips. Furthermore, surface roughness is another factor which increases overall surface area, resulting in increased oil uptake (Saguy and Pinthus, 1995).

2.13.4 Moisture Content

Several published papers deal with the relationship between moisture content and frying time. Gamble et al. (1987) showed that moisture loss was proportional to the square root of frying time. It is well established that oil absorption occurs after moisture is removed from the food during frying and a higher initial moisture content results in a higher fat uptake (Saguy and Pinthus, 1995). This is because oil essentially replaces the voids left by the water. Water loss and oil uptake have also been found to be affected markedly by the product's gel strength (Pinthus et al., 1992). Gamble et al. (1987) also proposed that most of the oil is pulled into the slice when it is removed from the fryer due to condensation of steam producing a vacuum effect.

2.13.5 Food Product Composition

For some products, the higher the initial fat content of the food, the greater is the amount of oil uptake; this has been shown for pie crusts and a European type of doughnuts called Berliners. However, contrary results were reported for several other products such as meat and fish (Saguy and Pinthus, 1995). Adding soy protein to cake doughnuts was shown to reduce oil uptake. A similar effect was described for

ovalbumin in frying batters (Mohamed et al., 1995). Addition of powdered cellulose and its derivatives have been shown to reduce oil uptake. Methyl cellulose was reported to be significantly more effective than powdered cellulose in reducing oil uptake in doughnut and falafel balls (Pinthus et al., 1992; Funami et al., 1999). Bouchon and Pyle (2004) also showed that type of starch is important for oil uptake during deep-fat frying of restructured potato chips. A product containing native potato starch as ingredient resulted in a much higher fat content chip when compared to a 100% potato flake base product.

2.13.6 Pre-Frying Treatment

Some pre-frying treatments have been shown to significantly reduce oil absorption during frying. Lowering the moisture content of the food prior to frying using microwave and hot-air treatment results in a reduction in the final oil content, whereas freeze-drying increases oil absorption (Gamble and Rice, 1987). On the other hand, post-treatment such as hot air drying have been shown to reduce absorption (Nonaka et al., 1977).

2.13.7 Surface Treatments

Some attention has been given to the use of hydrocolloid coating as a means of inhibiting oil absorption during frying. The usual approach is to incorporate the hydrocolloid in meat and chicken ball coatings. The film acts as a selective barrier for moisture removal and oil penetration. During frying, edible coatings form a thermally induced barrier between food and the frying medium. In addition, the edible film coatings provide stability and shape to the product, and reduce material losses from the product surface as well as oil penetration (Ateba and Mittal, 1994, Balasubramaniam et al., 1995; Balasubramaniam et al., 1996).

2.13.8 Gel Strength

Gel strength is mainly important in restructured food products. Both water loss and oil uptake have been shown to be affected markedly by the product's gel strength. Pinthus et al. (1992) studied the effect of gel strength of a restructured potato product on oil uptake. They found that both water loss and oil uptake at 170 °C was significantly lower at higher gel strengths. However, the effect of increased gel strength on lessening oil uptake could not be explained merely by considering the creation of a barrier, which simultaneously reduced water movement to the surface, rate of evaporation, and oil uptake (Saguy and Pinthus, 1995). Pinthus et al. (1992) suggested that other product characteristics (e.g., compressibility, porosity, internal structure) could be involved. Finally, Pinthus and Saguy (1994) found that the gel strength was independent of interfacial tension between a frying medium and the product, and suggested that the two properties should be evaluated separately.

2.13.9 Porosity

Porosity is a significant factor affecting oil uptake in deep-fat frying. Bouchon (2002) showed that the porosity of the crust is important for oil uptake in both potato cylinders and potato crisps. In addition, water loss is a crucial parameter to be assessed, as it gives an indication of the extent of porosity of the crust developed, allowing the oil to enter easily into the structure at the end of frying when product is removed from the oil (Bouchon, 2002). It can be stated that higher porosity implies greater oil uptake.

2.13.10 Crust

Crust is formed during most deep-fat frying process, and it is one of the most palatable characteristics of fried foods (Saguy and Pinthus, 1995). Crust formation is closely associated with fat distribution in the fried food. Pinthus et al. (1995) found

that crust oil uptake of fried potato product stopped when the crust yield strength reached a critical value of 210 to 240 kPa. Furthermore, the oil tended to concentrate more near the edges, corners, and broken "slots" of the crust (Saguy and Pinthus, 1995).