Chapter 1

Introductory Chapter: Some New Aspects of Colloidal Systems in Foods

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http://dx.doi.org/10.5772/intechopen.85298

1. Introduction

Food products usually showed the colloidal systems as emulsions, foams, gels, and dispersions. They are multicomponent systems containing different types of ingredients. Therefore, researches about food colloid are important; but first, we must be answered to below questions before starting. (1) How the physical properties of structure, stability, and rheology are influenced by the ingredient composition and formulation conditions? (2) How the interactions between various kinds of dispersed entities (e.g., particles, droplets, and bubbles) and macromolecules (proteins and polysaccharides) influence behavior in bulk fluid phases and at solid and liquid interfaces (air-in-water or oil-in-water)?

For these aims, many types of research are annually carried out for the understanding of how different classes of food ingredients control the physicochemical mechanisms determining overall stability and textural properties. Information on these model systems determined the reliable data about these colloidal systems, but not very reliant, because in the food products numerous components exist which influenced the quality and stability of final products. One of the main objectives of the colloid-based approach is the control of biopolymer interactions with the objective of fabricating well-defined nanoscale structures for controlled destabilization of colloidal systems [1, 2].

It should be noted that based on many papers presented at the 13th European Food Colloids Conference, almost all researches are focusing on four main areas: (i) structure and rheology of protein gels; (ii) properties of adsorbed protein layers; (iii) functionality from protein-polysaccharide interactions; and (iv) oral processing of food colloids. But nowadays, the behavior of dispersed systems within the human digestive systems has emerged as a major topic of research interest. Another outstanding influence on future food colloids research has a strong biomedical emphasis (the topic of controlled release and nutrient delivery) [3]. The development of colloid-based strategies to control delivery of nutrients during digestion in gastrointestinal is very important.

In this chapter, the progress in the field of ingredients, microstructure, and stability of food colloidal systems are discussed. Moreover, the application of new structured functional ingredients for the design of novel colloidal matrix (such as multilayer interfaces, multiple emulsion, gel-like emulsions, and so on) are reviewed. In this further, we will discuss: (i) classification and functions of colloidal systems in food; (ii) types of colloidal systems in food; and (iii) stability of colloidal systems.

A colloid system is a type of mixture in which one part is dispersed constantly throughout another. Colloid systems are usually formed when one part is dispersed through another, but does not combine to form a solution. Therefore, there are many types of colloidal systems that depend on the form of the two parts mixed together.

A colloidal system contains two separate phases: a dispersed phase (or internal phase) and a continuous phase (or dispersion medium). The part which is dispersed is known as the dispersed phase and is suspended in the continuous phase. Colloidal systems in food can be classified into different groups based on the states of matter constituting the two phases. Food colloids are sols, gels, emulsion, and foam. For example, egg white foam is a simple colloid system. Air bubbles (disperse phase) are trapped in the egg white (continuous phase) resulting in a foam. The detailed classification of colloidal systems in food is shown in **Table 1** [4].

Food colloids give structure, texture, and mouth-feel to many different food products; for example, jam, ice cream, mayonnaise, etc. Food colloid contains hydrocolloid that provides thickening, gelling, emulsifying, and stabilizing properties in food products [5].

Food hydrocolloids are high molecular weight hydrophilic biopolymers used as functional constituents in the food processing to modify microstructure, texture, flavor, and shelf-life. The term "hydrocolloid" comprises all the numerous polysaccharides that are obtained from plants, seaweeds, and microbial sources, as well as modified biopolymers made by the chemical or enzymatic treatment of starch or cellulose. One of the key functional roles of food hydrocolloids is in the preparation of emulsions and in the control of emulsion shelf-life. Most

System	Minor phase	Major phase	Products
Sol	Solid	Liquid	Raw custard, unset jelly
Gel	Liquid	Solid	Jelly and jam
Emulsion	Liquid	Liquid	Mayonnaise, milk
Solid emulsion	Liquid	Solid	Butter, margarine
Foam	Gas	Liquid	Whipped cream, whisked egg white
Solid foam	Gas	Solid	Meringue, bread, cake, ice cream

Table 1. Colloidal systems in food.

http://dx.doi.org/10.5772/intechopen.85298

hydrocolloids can behave as stabilizers (stabilizing additives) of oil-in-water emulsions, but sole a few of them can act like emulsifiers (emulsifying agents). The second functionality needs considerable surface activity at the oil-water interface, and therefore the capability to favor the development and stabilization of fine droplets throughout and next emulsification [6, 7].

2. Stability of colloidal systems

The most part of colloids are stable, but the two phases may separate during a period of time due to an increase in temperature or through physical force. Furthermore, they may become unstable after freezing or heating, especially if they contain an emulsion of fat and water. The details of the instability of food colloids are reviewed in further part.

2.1. Sols and gels

A sol can be defined as a colloidal dispersion in which a solid is the dispersed phase and liquid is the continuous phase. Gravy stirred custard and other thick sauces are some of the examples. While jelly is formed, gelatin is scattered into a liquid and heated to make a sol. As the solution cooks, protein molecules unwind developing a network which traps water and creates a gel.

If corn flour is mixed with water and heated, the starch granules absorb water till they rapture, after that starch granule disperses in the water and the mixture becomes more viscous and makes a gel after cooling. Additional types of gel are formed with pectin and agar. Pectin, a form of carbohydrate found in fruit, is used in the production of jam to help it set. Agar is a polysaccharide extracted from seaweed which is capable of forming gels. If a gel is allowed to stand for a time, it starts to “weep.” This loss of liquid is known as syneresis. The proper ratio of the ingredients is necessary to achieve the desired viscosity of the sols at a certain temperature.

Sols can be transformed into gels as a result of a reduction in temperature. In pectin gels, the pectin molecules are a major phase and the liquid is the scattered phase, whereas in pectin sol, the pectin molecules are a minor phase and the liquid is a major phase. Sols can be made as an initial step in the creation a gel. Jams and jellies produced using pectin are traditional cases that make a sol before the preferred structure.

2.2. Emulsions

Numerous natural and processed foods involve either relatively or entirely as emulsions or have been in an emulsified form at some time through their fabrication containing milk, cream, butter, margarine, fruit beverages, soups, batters, mayonnaise, cream liqueurs, sauces, desserts, salad cream, ice cream, and coffee whitener.

Emulsion products exhibit a wide variety of different physicochemical and organoleptic characteristics in appearance, aroma, texture, taste, and shelf-life. The processing of an emulsion-based food product with specific quality features is influenced by the selection of suitable raw materials (e.g., water, oil, emulsifiers, thickeners, minerals, acids, bases, vitamins, flavors, colorants, etc.) and processing situations (e.g., mixing, homogenization, pasteurization, sterilization, etc.).

An emulsion involves two immiscible phases (typically oil or water), with one of the liquids scattered as fine sphere-shaped droplets in the other. A system which contains oil droplets dispersed in an aqueous phase is termed an oil-in-water or O/W emulsion (e.g., mayonnaise, milk, cream, soups, and sauces). A system which involves water droplets scattered in an oil phase is termed as a water-in-oil or W/O emulsion (e.g., margarine, butter, and spreads) [8].

Multiple (or double) emulsions are multipart liquid dispersion systems well-known too as emulsions of emulsions, in which the droplets of one scattered liquid (water-in-oil or oil-in-water) are more scattered in another liquid (water or oil, correspondingly), making W/O/W or O/W/O. The innermost scattered droplets (hereafter called inner droplets or just droplets, while the droplets of the multiple emulsion will be named, for simplicity, the drops) in the multiple emulsion are disconnected from the external liquid phase by a film of another phase.

Although multiple emulsions are an emerging technology, only a few industrial products based on multiple emulsions exist in the marketplace. The main application of multiple emulsions is a protection system for the controlled release of active compounds. In the food industry, W/O/W emulsions are able to increase the solubility of specific active materials, solubilize oil-insoluble ingredients, and serve as protecting liquid reservoirs for molecules sensitive to outside environmental reactivity including oxidation, light, and enzymes, and act as entrapment reservoirs for covering off flavors and odors.

Applications in the cosmetics trade include aqueous preparations that provide a good "feel" and slow release of active materials or flavors, deposition of water-soluble agents onto the skin from wash-off systems. Most applications are related to the pharmaceutical industry, such as enhancing the chemotherapeutic effect of anticancer drugs, drug immobilization, treatment of drug overdoses, and protecting insulin from enzymatic degradation. However, the size of the droplets and the thermodynamic instability is a significant drawback of this technology. It seems that double-emulsion technology can now be applied in various areas, mainly in food, cosmetics, and pharmaceuticals [9, 10].

Emulsions are suggested as carriers of plant antioxidants in food systems that are discussed deeply in Chapter 2. In fact, plant antioxidants due to the natural sources and health-promoting product are very attractive in food science. So, information about the structure of plant antioxidants, degradation of them in food systems, physical and chemical stabilities of these systems are important for study in the future. In Chapter 3, the application of nanoemulsion in food science is discussed. Nanoemulsion is very attracting due to the advances of nanotechnology in the recent years. Nanoemulsion has been applied in functional foods and pharmaceutical industries. Therefore, nanoemulsion production with a novel technique and its stability is very important.

In general, emulsions are thermodynamically unstable and therefore tend to breakdown over time due to various physicochemical mechanisms. Therefore, stabilizers are used in emulsion formulations for improving their long-term stability, such as emulsifiers, texture modifiers, ripening inhibitors, and weighting agents. Emulsifiers (such as small molecule surfactants, phospholipids, proteins, polysaccharides, and other surface-active polymers) are typically amphiphilic molecules that have both hydrophilic and hydrophobic groups on the same molecule.

The most important polysaccharide emulsifiers in food applications are Arabic gum, modified starches, modified cellulose, pectin, and some galactomannans. The role of the emulsifier is to adsorb at the surface of the freshly formed fine droplets and so prevent them from coalescing with the near droplets to form larger droplets again. Mayonnaise is an example of a stable emulsion of oil and vinegar, when egg yolk (lecithin) may be used as an emulsifying agent.

Emulsions are usually formulated by a single type of emulsifier. But, in some cases, the quality and functional properties of emulsions can be improved by using a combination of several emulsifiers rather than the individual alone. Each of them has a unique molecular and physicochemical characteristic that can be applied for modulation the interfacial properties of emulsion droplets.

Novel or improved functional attributes can often be obtained by using emulsifier mixtures rather than single emulsifiers, for example, enhancements in antioxidant activity, flavor encapsulation, nutraceutical delivery, or textural attributes. Due to the increasing demand for clean-label products, utilization of natural emulsifier's mixtures can be recommended [11]. In addition, the new technique to conjugate proteins with polysaccharide by Maillard reaction arising in the controlled dry heating between the Ɛ-amino groups of proteins and the reducing end carbonyl groups of polysaccharides are established. The most remarkable characteristic of the resultant protein-polysaccharide conjugates is the outstanding emulsifying attributes which are preferred in comparison to commercial emulsifiers [12].

Moreover, wet-heating has been adopted to prepare protein-polysaccharide conjugate. Wet-heating mostly shortens the reaction time to only several hours at high temperature and short reaction time limits the Maillard reaction to initial stage to provide better browning control [13, 14].

2.3. Foams

Foams consist of small bubbles of gas (frequently air) scattered in a liquid, for example, egg white foam. As liquid egg white is whipped, air bubbles are included. The mechanical action leads albumen proteins to unfold and make a network, entrapping the air. If egg white is heated, protein coagulates and moisture is driven off. This creates solid foam, for example, a meringue. Ice cream, bread, and cake are other instances of solid foams.

3. Recent advances in food colloidal systems and recommendations

Recent interest from researches is the application of structural design principles for the fabrication of edible colloids with novel functional properties. This research activity is driven forward by an increasing recognition within the food industry of the value of colloidal systems as delivery vehicles for nutrients and flavor compounds.

In Chapter 5, the role of electrostatic and steric forces in food colloids and their stability are discussed. Based on biopolymer interaction, a combination of protein and polysaccharide functionality for production of the novel biopolymer with enhanced functional properties is deeply studied. Proteins and polysaccharides are two groups of hydrocolloids that are widely used in food formulations simultaneously. These macromolecules are known to play important physicochemical roles, such as thickening, stabilizing, gelling, emulsifying properties, etc., in food products. Interactions between two hydrocolloids play an important role in the structure and stability of processed foods and depend not only on the physicochemical properties of proteins or polysaccharides alone [15–17].

Nowadays, the intelligent manipulation of protein and polysaccharide interactions provides opportunities for the design of new ingredients and interfacial structures with applications in the food and pharmaceutical industries.

So, food scientists can control the microstructure, texture, and shelf-life of edible colloidal systems with attention to theirs. Protein-polysaccharide interactions could play a key role in the nanoscale engineering of novel foods designed to address the widespread health concerns associated with obesity problem and the release of specific nutrients [18].

In addition, nowadays multilayer interfaces are very interested in food industries. Multilayer interfaces in food colloids typically consist of adsorbed layers of proteins and polysaccharides made by the sequential or simultaneous deposition of oppositely charged macromolecules at the surface of emulsion droplets [19].

With the advancement of nanotechnology in different fields such as food industry, some researchers studied various nanoencapsulation techniques for controlled and protection of some bioactive ingredients including pharmaceuticals and food bioactive components with the high bioavailability. Based on the main applied ingredients/equipment for the formulation of encapsulation systems, nanocarriers are classified into five groups: (1) lipid-based nanocarriers (such as nanoemulsions, nanoliposomes, and nanolipid carriers); (2) nanostructured colloids nanocarriers (such as caseins, cyclodextrins, and amylose); (3) nanocarriers produced by special equipment such as electro-spinning/spraying, nano-spray dryer, and micro/nanofluidics systems; (4) biopolymers nanoparticles nanocarriers (such as single biopolymer nanoparticles, biopolymer-biopolymer complexation, nanogels of alginates, whey, soy proteins, and chitosan, nanotubes, or nanofibrils); and (5) miscellaneous nanocarriers (such as nanoparticles made from chemical polymers, nanostructured surfactants, inorganic nanoparticles, and nanocrystals). Hence, it is possible to choose appropriate nanodelivery systems based on the solubility and predicted functionality of bioactive components.

In last few years, there has been many published studies on the nanoencapsulation of different food ingredients such as phenolic compounds and antioxidants, natural food colorants, antimicrobial agents and essential oils, minerals, flavors, essential fatty acids and fish oil, and vitamins [20]. Active compounds such as antioxidants and antimicrobials are added into the food formulation for aims of quality loss and microbial safety management. But there are limitations such as pro-oxidation in lipid foods and compliance of regulatory maximum allowable concentration. Therefore, controlled release packaging (CRP) is a novel technology that is applied for the package with release active compounds in a controlled trend to improve safety and quality for food products during storage. Research in controlled release packaging focused on released systems such as active compounds from the package, non-releasing antimicrobials or antioxidants, oxygen absorbers, and free-radical scavengers those grafted on to packaging materials [21].

One developing area in the application of colloidal dispersions is the manufacture of functional foods. Functional foods are becoming progressively favorite among consumers as the result of improved knowledge of functional components and their influence on human wellbeing and biological functions. The customers would like to overcome health problems such as cardiovascular problems and obesity through consuming foods rather than drugs. The plan of functional foods for the delivery of nutraceuticals and micronutrients is a great technological challenge. Colloidal delivery systems are actually found in nature. Casein, for example, is a very illustrative instance of a natural colloidal delivery system for calcium. In milk, calcium is cleverly "engineered" into porous casein colloidal elements of sizes lesser than approximately 500 nm [22]. In Chapter 4, the nanostructured colloids in various areas of food science are discussed.

Nanostructured colloids can be naturally present in food or they can be synthetically manufactured. Some examples of natural nanostructured colloids include casein micelles and β-lactoglobulin in milk, and in the case of synthetically manufactured colloids are metal oxide nanoparticles and clay. Synthetically manufactured nanostructures are added to enhance solubility, improve bioavailability, biologically active compounds protection, increasing shelf-life, color, flavor, and add nutritional value.

The industrial sciences have been of great attention to the development of new bio-based structures with potential in innovative applications. Structures with gel-like behavior are usually used in the cosmetic, pharmaceutical, and food industries for the aim of controlling the physical properties of final products. In the food industry, words like oleogels and organogels have been increasingly used. Oleogels are new emulsion-based structure that can be used to control phase separation and decrease the mobility and migration of the oil phase, providing solid-like properties without using high levels of saturated fatty acids as well as to be a carrier of bioactive compounds. In this area, it can be used as the food grade and bio-based structurants for producing edible oleogels with fat replacement and structure-tailoring functionality [23].

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