RESEARCH ARTICLE OPEN ACCESS

Emulsion and it's Applications in Food Processing – A Review

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ABSTRACT
An emulsion is a heterogeneous system consisting of atleast one immiscible liquid dispersed in another in the form of droplets. Emulsions are classified based on the nature of the emulsifier or the structure of the system. The range of droplets size for each type of emulsion is quite arbitrary. Macro emulsions are the most common form of emulsions used in food industries than nano and micro emulsions. There are several methods are possible and a wide range of equipments are available for emulsion formations. These methods include shaking, stirring and injection, and the use of colloid mills, homogenizers and ultrasonics. The unique nature of emulsions with a narrow size distribution of different sized droplets has number of applications in food industries including bakery products, dairy, candy products, meat products and beverages. Still most applications are waiting for commercial exploitation.
Key words: Applications, Colloid mills, Emulsions, Homogenizers, Ulrasonics.

I. INTRODUCTION

The definition of an emulsion has continued to evolve since the 1930s. Becher (1957),developed an elaborate definition from several previous authors. ''An emulsion is a heterogeneous system, consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, whose diameter, in general, exceeds 0.1 μm. Such systems possess a minimal stability, which may be accentuated by such additives as surface-active agents, finely divided solids, etc.'' Freiberg et al. (1969) elucidated the significance of liquid crystalline phases on emulsion stability. This was reflected in the IUPAC-IUB (1972) definition of an emulsion: ''In an emulsion, liquid droplets and/or liquid crystals are dispersed in a liquid.'' Sharma and Shah (1985) defined both micro- and macroemulsions, differentiating them on the basis of size and stability. Macroemulsions were defined as''mixtures of two immiscible liquids, one of them being dispersed in the form of fine droplets with (a) diameter greater than 0.1 μm in the other liquid. Such systems are turbid, milky in color and thermodynamically unstable.'' Microemulsions were defined as ''clear thermodynamically stable dispersions of two immiscible liquids.'' The dispersed range consists of small droplets in the range of 100–1000 A˚ . Food macroemulsions are unstable systems, even with the addition of emulsifiers.

Emulsifiers are added to increase product stability and attain an acceptable shelf-life. The function of an emulsifier is to join together oily and aqueous phases of an emulsion in a homogeneous and stable preparation (Waginaire, 1997). The main characteristic of an emulsifier is that it contains in its molecule two parts. The first part has a hydrophilic affinity, while the second has a lipophilic affinity.

Emulsifier selection is based upon final product characteristics, emulsion preparation methodology, the amount of emulsifier added, the chemical and physical characteristics of each phase, and the presence of other functional components in the emulsion. Food emulsifiers have a wide range of functions. The most obvious is to assist stabilization and formation of emulsions by the reduction of surface tension at the oil–water interface, to alter the functional properties of other food components and third function is to modify the crystallization of fat. This paper reviews the types of emulsions, emulsion formation and its applications in food industries.

II. CLASSIFICATION OF EMULSIONS

Emulsions may be classified according to the nature of the emulsifier or the structure of the system. A number of different terms are commonly used to describe different types of emulsions and it is important to classify these terms (McClements, 2010; Solan et al, 2005; Maron et al, 2006; Tadros et al., 2004). The range of droplets size for each type of emulsion is quite orbitary and is defined in terms of the physical and thermodynamic properties of emulsions. A conventional emulsion, also known as a macroemulsion, typically has a mean droplet diameter (MDD) between 100nm and 100m. Macroemulsions are the most common form of emulsions used in food industry and are found in a variety of products, including milk, beverages, mayonnaines dips, sauces and desserts. Macroemulsions are prone to physical instability (Eg: gravitational separation, foculation and coalescence). Especially when exposed to environmental stresses(Peter, 2009; Djordjevic et al, 2007; Klinkesorn et al, 2005; Aoki et al, 2005).

Nanoemulsion are dispersions of nanoscale droplets with a MDD between 20-100nm. It is worth nothing that in old days, "microemulsion" was also used to refer to emulsions comprised of submicron droplets(Landfester et al, 2000; Choi et al, 1985 and Tang et al, 1991). In contrast to nanoemulsions, miniemulsion have droplets in the range from 100nm to 1m. Because miniemulsions and macroemulsions are thermodynamically unstable.

Microemulsion is a thermodynamically stable system and forms spontaneously with droplet size between 5 to 50nm(McClements, 2010). Nanoemulsions are the same as microemulsions since they both typically contain oil, water and surfactant and also have similar MDD. However, the two systems are very different since nanoemulsions are formed by mechanical slear and microemulsion(Moulik and Paul, 1998; Flanagan and Singh, 2006; Zhang et al, 2008; Garti et al, 2004; Fanun, 2009). The main difference between microemulsion and minscale emulsion is not composition but rather thermodynamic(Maron et al, 2006; Whitesides, 2002).

III. EMULSION FORMATION

The first step in the formation of a stable emulsion is dispersion of one liquid phase in another liquid phase. A critical factor in that emulsification process is the formation of a monomolecular layer at the lipid/water interphase by the emulsifier. During emulsion formation there is a large increase in surface area (up to several thousandfold), which is dependent upon the number and size of the droplets. To form and disperse these droplets,
a substantial amount of energy or work must be supplied. Since emulsifiers reduce the surface tension, the addition of emulsifiers reduces the amount of work that must be done to form the emulsion. The most common method of emulsion formation is the application of mechanical energy via vigorous agitation.

The emulsifier is first dissolved in the aqueous or organic phase depending on the solubility of the emulsifier and on the type of emulsion desired. Next, sufficient agitation to cause surface deformation and large droplet formation is applied during the addition of one phase to the other. The next step is disruption of the droplets. To form a stable emulsion and prevent coalescence, sufficient emulsifier must be available to adsorb at the
aqueous/organic interphase. The emulsifier lowers the Laplace pressure, which facilitates droplet deformation and disruption (Walstra, 1983). After droplet formation, the emulsifier partitions into the interphase of the aqueous/organic system stabilizing the emulsion.

Droplet size, which is directly related to the emulsification procedure, is also dependent on
the amount of emulsifier added, the type of emulsifier, and the emulsification temperature.

There are several possible methods for emulsion formation and a wide range of equipment is available for emulsion formation. These methods include shaking, stirring, and injection, and the use of colloid mills, homogenizers, and ultrasonics.

One problem of key importance is the scale-up from laboratory to pilot plant to manufacturing (Lynch and Griffin, 1974). It is important to closely simulate manufacturing conditions during pilot plant preparation of the emulsion, particularly if this is not possible on a laboratory scale. On a laboratory scale, the use of a blender to prepare an emulsion may result in the application of more energy and a much faster rate than is possible in a
manufacturing situation. If at all possible, laboratory equipment as well as pilot plant
equipment should be of the same design as the production equipment. A motor-driven propeller or a hand-driven homogenizer would provide a much more realistic simulation of actual manufacturing conditions than a blender.

Colloid mills emulsify based on the shearing action imparted to the liquid by a highspeed rotor moving within a fixed stator. The stator and rotor are separated by a very small gap (Becher, 1957). Clearance between the rotor and stator may be as small as 0.001in. Many manufacturers, like Chemicolloid Laboratories (Garden City Park, NY), utilize grooved rotors and stators in their design, along with an adjustable clearance between the rotor and stator. Greeco offers a colloid mill with grooving and an adjustable gap that they recommend over their high speed mixer for emulsions of smaller droplet size, like mayonnaise. The gap is adjusted depending upon the type of emulsion. One disadvantage of a very small gap size is reduced throughput. APV Gaulin (Everett, MA), a colloid mill manufacturer, suggests that the colloid mill is best suited to high-viscosity products with high ratios of oil to water, like mayonnaise. With mayonnaise, moderately small droplet sizes are best. With too small a droplet size and the concomitant increased surface area, the total surface area of the emulsion will likely exceed the capacity of the added emulsifier, significantly reducing product stability.

A familiar piece of emulsifying equipment is the homogenizer due to its widespread use for the homogenization of milk. Homogenizers emulsify by forcing the product through a small orifice under substantial pressure. The most likely mechanism for droplet size reduction is the dual effect of cavitation and turbulence. As the orifice size is decreased and the pressure is increased, the size of the dispersed phase droplets is decreased. In order to utilize the homogenizer most effectively, one manufacturer suggests that the product entering the homogenizer should be premixed so the particle size is less than 20 μm in diameter. Another possibility is the use of either multistage homogenizers or multiple passes through a single homogenizer to insure small, uniform droplets. The homogenizer is, of course, recommended for milk homogenization. It is also recommended for processing dispersions such as catsup and tomato sauce, for producing flavor and beverage emulsions, and for the production of frozen whipped toppings.

Ultrasonic emulsification is the treatment of liquids with high-frequency vibrations to produce high-intensity cavitation. Sound waves move through the liquid, compressing and stretching it, which results in cavity or bubble formation within the liquid. Upon collapse of the bubbles tremendous shear forces are generated. The ultrasonic process can be influenced by controlling static pressure, temperature, amplitude of vibration and flow rates.

According to Branson (Danbury, CT) and Sonic (Stratford, CT), two of several ultrasonic equipment manufacturers, there are both limitations and advantages to ultrasonic emulsifying equipment. The equipment is not particularly effective for large volumes or for highly viscous products. Advantages include lower capital and operating costs, no premixing requirement, lower maintenance, and easier cleaning relative to homogenizers.

IV. EMULSIONS IN FOOD INDUSTRIES

The unique nature of emulsions as thermodynamically stable dispersions with a narrow size distribution of different sized droplets has made them suitable for a number of applications in food industries.

Cereal-Based Products

A review by Schuster and Adams (1984) and another by Stampfli and Nersten (1995) covered research on emulsifiers with respect to baked goods and included an excellent discussion on the mechanism of emulsification, the interaction of emulsifiers with starch, and a wide range of applications.

Emulsifiers can function as dough conditioners. Advantages attributed to dough conditioners include (1) improved tolerance to variations in flour and other ingredient quality, (2) doughs with greater resistance to mixing and mechanical abuse, (3) better gas retention resulting in lower yeast requirements, shorter proof times, and increased baked product volume, (4) increased uniformity in cell size, a finer grain, and a more resilient texture, (5) stronger sidewalls, (6) reduced shortening requirements, and (7) improved slicing (Dubois, 1979; Rusch, 1981; Brummer et al., 1996).

Gawrilow (1979) developed a mathmetical model to predict the effect of added emulsifiers on bread quality. Several different types of bakery products, in addition to bread produced via conventional methods, benefit from added emulsifiers, including white bread produced by a highly mechanized process, buns and rolls, yeast-raised sweet rolls and doughnuts, plus variety breads that contain a significant portion of nonwheat flour components (Schuster and Adams, 1984; Stampfli and Nersten, 1995).

Certain emulsifiers also function as crumb softeners, another type of dough conditioner.

The soft crumb, a characteristic of freshly baked bread, can be retained longer if the appropriate emulsifiers are added. Crumb firming, associated with staling and starch retrogradation, can be delayed for 2–4 days with the addition of emulsifiers (Knightly, 1968). Emulsifiers are thought to reduce the rate of water migration and hence, staling, by complexing with the starch and adsorbing onto the starch surface (Pisesookbunterng and D'Appolonia, 1983). In fact, the amount of lipid complexation that occurs with amylase correlates well with the crumb softening effect in bread (Krog and Jensen, 1970; Lagendijk and Pennings, 1970).

Lorenz et al. (1982) evaluated several emulsifiers for their effect on crumb hardness. Of the eleven commercial sources of emulsifiers tested, four were most effective at 10 and 25°C: propylene glycol mono- and diesters, ethoxylated mono- and diglycerides, polyoxyethylene sorbitan monostearate, and succinylated monoglycerides. All of the emulsifiers tested, except hydroxylated lecithin, were equally effective at 40 and 50°C.

Diacetyl tartaric acid esters of monoglycerides (DATEM), a widely used emulsifier in Europe for bread products, appears to act as a dough strengthener and a crumb softener. It also improves loaf volume and delays staling (Hoseney et al., 1976; Rogers and Hoseney, 1983; Lorenz, 1983) and shows synergistic activity with monoglycerides (MGL) on gassing power (Armero and Collar, 1996). Lorenz (1983) suggested that the use of DATEM may increase as the sale of variety breads increases in the United States, since DATEM is particularly useful in European type hearth breads, which are not cooked in pans. Addition of diacetyl tartaric acid esters of mono- and diglcyerides improves the distribution of shortening within the dough. Another advantage is that the proof volume of weak doughs is affected to a greater degree than that of strong doughs. While the cost of DATEM relative to monoglycerides has delayed extensive use, the price difference has decreased (Walker, 1983). DATEM has a more pronounced effect than monoglycerides on crumb softness, loaf volume, and texture, which offsets some of the price difference.

Cake volume can be increased upon addition of several different emulsifiers, including diacetyl tartaric acid esters of monoglycerides, glycerol fatty acid esters, and calcium stearoyl-2-lactylate. Emulsifier addition to cake mixes facilitates increased substitution of sucrose with high-fructose corn syrup (Hartnett, 1979). Fructose causes starch gelatinization earlier during baking, relative to sucrose, reducing cake volume, grain size, textural quality, and shelf-life. Emulsifiers increase the gelatinization temperature offsetting the effect of the high-fructose corn syrup. Emulsifiers have three primary functions in cake: (1) to facilitate air incorporation, (2) to disperse shortening in smaller particles to allow the maximum number of air cells, and (3) to improve moisture retention (Painter, 1981; Flack, 1983). Flack (1983) indicated the most commonly used emulsifiers in cake include monoglycerides, lactylated monoglycerides, and polysorbates. Seward and Warman (1984) developed a lipophilic emulsifying system for cake mixes that contained monoglycerides, propylene glycol monoesters, polyglycerol esters, and lactylated monoglycerides.

Cookie characteristics (volume, top grain, and, particularly, spread ratio) can be improved with the addition of the appropriate emulsifier. Tsen et al. (1973) found that several emulsifiers affected cookie characteristics favorably, including sodium stearoyl fumarate, sodium stearoyl lactylate, sucrose fatty acid esters, polysorbates, sorbitan fatty acid esters, and ethoxylated monoglycerides. Tsen et al. (1975a) also found that emulsifiers could alter the effect of hard wheat flours such that hard wheat flour could be substituted for soft wheat flour. Like bread, the effect of nonwheat protein addition to cookies can be minimized by the addition of emulsifiers. Cookie shelf-life can also be increased with addition of emulsifiers (Hutchison et al., 1977). Emulsifier addition to cookie mix can improve the spread ratio, cooking surface release, and texture of cookies (Rusch, 1981). However, Breyer and Walker (1983) found that the addition of sucrose esters had a negligible effect on cookie quality.

The interaction of emulsifiers with starch alters the effect of heat on starch. Puddings, for example, were said to have increased freeze–thaw stability and increased resistance to retort processing, while starch-based sauces have improved freeze–thaw stability and increased stability during holding at high temperatures (Rusch, 1981).

Flat bread products are consumed extensively in the Middle East, North Africa, and the Indian subcontinent. Like other bread products, the flat breads will stale upon storage. Addition of sodium stearoyl-2-lactylate and monoglycerides reduced the degree of firmness upon storage of flat breads (Maleki et al., 1981). The addition of sucrose esters to chapaties, a flat bread product, allowed the substitution of 40% of the whole wheat flour with nonglutenous flour (e.g., corn, sorghum, millet, and soy) with only a slight loss in quality (Ebeler and Walker, 1983). This would facilitate soy flour fortification of chapaties to improve the nutritional quality of the product.

Dairy Products:

Ice cream is both a frozen foam and an emulsion. Protein and polar lipids (lecithin) found in milk function as surfactants in ice cream. However, these naturally occurring components are usually supplemented with additional emulsifiers to make ice cream. Emulsifiers in ice cream improve fat dispersion, facilitate fat–protein interactions, control fat agglomeration, facilitate air incorporation, impart dryness to formed products, confer smoother texture due to smaller ice crystals and air cells, increase resistance to shrinkage, reduce whipping time, and improve melt-down (Flack, 1983; Walker, 1983).

Bayer et al. (1997) reported that a polysorbate 80 blend with monoglycerides and diglycerides, 40% alpha-monoglyceride, 70% alpha-monoglyceride, and lecithin increased the consistency of viscosity of low fat ice cream mix and reduced whipping times and ice crystal sizes. These emulsifiers were found to increase stability to heat shock and improved the body and texture of low fat ice cream.

Ice cream is an O/W emulsion, but the monoglycerides used in ice cream would be classified as W/O emulsifiers due to their low HLB values, suggesting their function in ice cream is not simply emulsification (Berger, 1976). The monoglycerides improve foamability, impart solidity, and improve the shape-retaining characteristics of the frozen product. The improved foamability is due to interaction of the emulsifier with milk proteins.

Berger (1976) found that the interfacial tension between water and oil in the presence of 0.1% casein was substantially reduced when monoglycerides were added. This same effect did not occur upon addition of Tween 60. Berger (1976) suggested that a complex between casein and the monoglycerides is formed altering the tertiary structure of casein such that partial denaturation occurred. The improved shape-retaining characteristics and solidity attributed to emulsifiers is likely due to the partial destabilization of the fat emulsion (Berger, 1976) and agglomeration of the fat globules (Keeney and Kroger, 1974). Both the monoglycerides and the polyoxethylene sorbitan fatty acid esters are effective.

Flack (1985) found that mono- and diglycerides, citric acid esters of monoglycerides, lactic acid esters of monoglycerides, and distilled monoglycerides affected the whippability and foam stability of dairy whipping cream that had been pasteurized at 80°C and homogenized at 1000 psi. Lactic acid esters produced a stable foam with high overrun that was substantially different from a fresh whipped cream, while a mixture of citric acid esters and distilled monoglycerides produced a foam similar to that of fresh whipped cream.

Pearce and Harper (1982) developed a procedure for the evaluation of emulsion stability for liquid coffee whiteners upon addition to hot coffee. They found that if the emulsion was particularly unstable, coagulation occurred. However, with the addition of the correct mixture of emulsifiers, feathering could be completely eliminated. Cheese yield can be increased with the addition of lecithin. Lecithin was added in quantities of 0.001–0.066% by weight of the milk (Bily, 1981).

Candy Products:

The elimination of ‘‘bloom,’’ i.e., the transition of fat crystals from the alpha and beta′ configuration to the less desirable beta configuration, is a key reason for the addition of emulsifiers to candy products. Emulsifiers can be used as crystal structure modifiers in mixtures of triglycerides (Anonymous, 1983). Certain emulsifiers can also be used to control product viscosity in cream fillings and in chocolates. The conversion of the alpha form of stearic acid (Garti et al., 1982a) and tristearin (Garti et al., 1982b) to the beta form can be partially inhibited by the addition of sorbitan esters (Spans) and ethoxylated sorbitan esters (Tweens). Garti et al. (1986) also studied the effect of Spans and Tweens on polymorphic transitions in cocoa butter, suggesting that these emulsifiers might be effective in preventing chocolate bloom. Emulsifiers are often used with both semisweet and milk chocolate. Emulsifiers aid in processing by reducing the weep or exudate that occurs with heavy sugar pastes during processing (Riedel, 1985). Rubenstein et al. (1980) prepared a marshmallow-based frozen confectionary product with 0.2 to 0.8% emulsifier with an HLB between 3 and 9.

Ogawa et al. (1979) used emulsifiers (sucrose fatty acid esters, sorbitan fatty acid esters, glycerol fatty acid esters, or propylene glycol fatty acid esters) to improve shelf stability of center-filled chewing gum. The emulsifiers are added to the flavored liquid center at 0.01 to 0.5% by weight. Polyglycerol esters are used in coatings for confectionary products (Herzing and Palamidis, 1984).

Miscellaneous

Emulsifiers have been utilized in the production of meat analog products. Howard (1980) used emulsifier mixtures selected from the group consisting of polyglycerol fatty acid monoesters, monoacylglycerol esters of dicarboxylic acids, sucrose esters of fatty acids, polyol monoesters of fatty acids, and phospholipids to prepare meat analogs. Haggerty and Corbin (1984) used phospholipids to prepare filled meat products containing substantial amounts of both meat and texturized soybean protein. Emulsifiers are used in the formulation of flavor emulsions, although the available literature is rather limited. Chilton and Peppard (1978) evaluated several mixtures of Spans and Tweens to determine the optimum for the stabilization of hop oil emulsions. For those interested in flavor applications, recommendations should be solicited from companies that sell emulsifiers.

Margarine exists as a W/O emulsion for only a short period of time prior to chilling, at which time the emulsion is converted to a dispersion of water in a semisolid fat phase (Krog et al., 1985). Upon solidification, product stability is greatly enhanced, since coalescence is essentially eliminated. Emulsifiers fulfil three functions in margarine: (1) assistance in emulsion formation, (2) modification of crystal structure in the vegetable fat, and (3) antispattering. Typically, a mixture of lecithin or citric acid monoglycerides and monoglycerides are used. To reduce sandiness and ‘‘oiling out’’ in margarine due to recrystallization, emulsifiers can be added (Krog et al., 1985). The emulsifiers prevent recrystallization by slowing down the polymorphic transition rates (Dorota, 1996; Paola et al., 1996).

Mayonnaise is an O/W emulsion containing a high percentage of oil (_70%). Due to the large percentage of fat, coalescence, rather than creaming, is the primary problem (Jaynes, 1985). Different protein sources are utilized because of their effectiveness in reducing coalescence. The manufacturing procedure for mayonnaise is very critical since the high percentage of oil favors a W/O emulsion rather than an O/W emulsion (Krog et al., 1985). Lecithin, contained in the added egg yolk, is usually the only emulsifier added. However, the vegetable oil may contain emulsifiers added to inhibit crystallization, e.g., ethoxylated sorbitan monooleate and monostearate (Anonymous, 1983). To inhibit cloud formation in salad dressings and

salad oils, emulsifiers can also be added. To improve wetting characteristics in instant cocoa drinks, the powder is agglomerated.
Lecithin will facilitate agglomeration during spray-drying. During the spray-drying process the hydrophobic portion of the emulsifier will dissolve in the cocoa butter, orienting the hydrophilic portion of the phospholipid toward the surface of the particle (Van Nieuwenhuyzen, 1981). The increased affinity of the cocoa powder for water aids dispersion and wetting. Emulsifiers are often used in peanut butter. The addition of an emulsifier to peanut butter can inhibit oil phase separation.

V. CONCLUSION

Emulsions have a long history of use and are widely used in many products encountered in everyday life. Importance of emulsion in food industries justifies a great deal of basic research to understand the origin of instability and methods to prevent their break down. Research is needed in the area of developing highly technology oriented machineries for emulsion formation from lab scale level to pilot scale level. Understanding the theoretical considerations in emulsion formulation and having the ability and proper instrumentation to fully characterize and monitor stability of an emulsion system is highly beneficial to provide a superior product in a more time efficient manner.

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