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REVIEW



Functionality of bovine milk proteins and other factors in foaming properties of milk: a review

Thao M. Ho^{*} , Bhesh R. Bhandari , and Nidhi Bansal 

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ABSTRACT

For many dairy products such as cappuccino-style beverages, the top foam layer determines the overall product quality (e.g. their appearance, texture, mouthfeel and coffee aroma release rate) and the consumer acceptance. Proteins in milk are excellent foaming agents, but the foaming properties of milk are greatly affected by several factors such as the protein content, ratio of caseins to whey proteins, casein micelle size, pH, minerals, proteolysis, presence of low molecular weight compounds (lipids and their hydrolyzed products) and high molecular weight compounds (polysaccharides); milk processing conditions (e.g. homogenization, heat treatment and aging); and foaming method and temperature. These factors either induce changes in the molecular structure, charge and surface activity of the milk proteins; or interfere and/or compete with milk proteins in the formation of highly viscoelastic film to stabilize the foam. Some factors affect the foamability while others determine the foam stability. In this review, functionality of milk proteins in the production and stabilization of liquid foam, under effects of these factors is comprehensively discussed. This will help to control the foaming process of milk on demand for a particular application, which still is difficult and challenging for researchers and the dairy industry.



KEYWORDS

Foamability; foam stability; protein functionality; casein; whey protein

Introduction

Foam is an emulsified system in which air bubbles are dispersed in the continuous phase. Normally, the dispersed gas is atmospheric air, but in some cases (e.g. aerosol cream) inert gases (CO₂, N₂ or N₂O) are utilized. The continuous phase can be liquid or (semi-) solid by which foams are classified into liquid-based or solid-based foams, respectively Walstra (1989). However, in the scope of this review, only liquid-based foams are described. Typical products for liquid-based foams are cappuccino-style drinks such as cappuccino, macchiato and latte. These products differ in their ratio of extracted coffee (espresso), hot milk and foam (Hidden et al. 2012). The foam layer on the top is a critical element to the product quality due to its light and soft texture which is highly appreciated by consumers for notably its appearance prior to consumption, and for a smooth mouthfeel, creaminess and tactile sensations during consumption. Moreover, such as foam layer helps to slow down the release rate of aroma in coffee (Khezri, Shahriari, and Shahsavani 2017; Dold et al. 2011). The desirable foam should have small (micro-size) and uniform size of air bubbles, and stable for at least 10 min during which half a cup of coffee is typically consumed (Ho et al. 2019; Xiong et al. 2020). In most coffee shops, foam is typically prepared by injection of steam into milk through very small openings or nozzles which are placed just below the milk surface. The

steaming process is completed as the temperature of the foaming milk reaches approximately 60–65 °C. This temperature is desirable for dispersing hot beverages like cappuccino-style drinks. During foaming process, after the air is incorporated into the bulk of the liquid, air bubbles are formed and are likely to coalesce to minimize the surface area due to a high surface tension of water in the system. However, the presence of appropriate surfactants in the foaming system helps to stabilize air bubbles as they adsorb rapidly onto the air-liquid interface to reduce the surface tension and to promote the formation of elastic interfacial film surrounding the air bubbles (Kinsella 1981). Milk proteins are excellent foaming agents, even at a concentration as low as 0.02 ppm for caseins, due to their distinctive structure and properties (Kinsella and Morr 1984). Therefore, during several processing unit operations of milk, such as transportation of milk in the pipe systems for heat treatment processes, filling of milk into containers, or reconstitution of milk powders into water, there is unavoidable foaming of milk, which leads to the product loss or serious engineering problems. Over past several decades, many studies have been done and many general principles are well known, but controlling foaming process of milk on demand to maintain the consistency of product quality is still a difficult task for researchers and the dairy industry. Foam is a multi-phase and multi-component system, and foaming process is

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Table 1. Differences in properties of caseins and whey proteins (Fox 2003; Mulvihill and Ennis 2003).

Properties	Caseins	Whey proteins
Physical state in milk	Large colloidal aggregates (micelles)	Monomers or as small quarternary structures
Particle size	Large (micelles, average 120 nm, molecular weight $\sim 10^8$ Da)	Small (molecules; molecular weight $\sim 1.5\text{--}8.0 \times 10^4$ Da)
Solubility at pH = 4.6	Insoluble	Soluble
Rennet coagulation	Yes	No
Molecular structure	Flexible without stable secondary and tertiary structures	Globular with disulfide bridges and tertiary structure
Coagulability by limited proteolysis	Yes	No
Heat stability	High	Low
Ion binding ability (Ca^{2+})	Yes	No

determined by numerous factors, ranging from milk source, quality and composition of milk to processing conditions or even seasonality. Although there are few review papers about foaming of milk available in literature, they are exclusive to effects of milk composition and processing conditions (Huppertz 2010) and general mechanisms of formation and stabilization of solid-based and liquid-based foams of plant and animal proteins (Narsimhan and Xiang 2018). This review emphasizes on the functionality of bovine milk proteins and other factors in of liquid milk. It provides a current update on the latest research about foaming behavior of bovine milk and factors that affect it.

Milk proteins and their properties relevant to foaming

In bovine milk, total protein content is about 3.5% (w/w) with two major types of proteins, namely caseins and whey proteins, and other minor groups of proteaceous materials such as milk fat globule membrane proteins and indigenous milk enzymes (Davoodi et al. 2016). Caseins represent about 80% of the total protein and include three major subunits: α_s -, β - and κ -caseins with an approximate weight ratio of 3:2:1. These casein subunits are disordered and flexible proteins. The uneven distribution of serine phosphate, carboxyl and hydrophobic amino acid residues along polypeptide chains provides them with a very amphophilic nature. These properties, together with the high content of randomly distributed proline residues make caseins prone to reversible intermolecular interactions *via* hydrophobic and ionic bondings, which is a function of pH, Ca^{2+} ion and temperature (Lee, Morr, and Ha 1992). In addition, because of having cysteine groups, the subunits, such as α_{s2} - and κ -casein, offer caseins with ability to interact with other proteins *via* disulfide bonding. It was reported that among casein subunits, β -casein exhibited the greatest ability to reduce surface tension and produce foam, followed by α_s -casein and then κ -casein (Lorient, Closs, and Courthaudon 1989). However, β -casein foam was the least stable as compared to α_s - and κ -casein foam due to lack of tertiary structure and intermolecular interactions.

Meanwhile, whey proteins account for approximately 20% of the total protein content and are obtained from processes where caseins are precipitated out or removed by filtration or centrifugation. They mainly consist of two major proteins: α -lactalbumin and β -lactoglobulin, accounting for about 70–80% of the total whey proteins. The major whey proteins exist as compact and globular proteins with

their hydrophobic residues buried, as far as possible, within the molecules, and are highly susceptible to heat induced denaturation and intermolecular disulfide bonding (Lee, Morr, and Ha 1992). With these characteristics, whey proteins are less effective than caseins in decreasing interfacial tension and subsequently foaming. As absorbed on the interface, whey proteins unfold only partially (retaining a considerable portion of their secondary structure), resulting in formation of viscous films to resist to air bubble collapse. Thus, whey protein foam is typically more stable than casein foam (Kamath 2007).

The dissimilarities in the molecular structure and properties of caseins and whey proteins result in their differences in foaming properties. These differences are summarized in Table 1 (Fox 2003; Mulvihill and Ennis 2003). The content and composition of milk proteins greatly vary depending on several factors such as climate conditions (e.g. temperature, environment and season), disease of the glands, parity, breed (e.g. genetics), nutrition (e.g. feed) and stage of lactation (DePeters and Cant 1992).

Mechanisms of formation and stabilization of liquid-based foams

Theoretically, any activities introducing gas (air) into the bulk of liquid could be utilized to produce foam, such as steam injection, air injection, shaking, sparkling, bubbling, mixing, agitating, supersaturating, whipping, beating or even pouring (Huppertz 2010; Kamath 2007; Walstra 1989; Wilde and Clark 1996). Together with air incorporation, these actions provide surfactants present in the system with energy to diffuse and adsorb onto the interfacial regions to reduce surface tension and facilitate the formation and stabilization of air bubbles (Huppertz 2010; Kinsella 1981). Role of milk proteins in formation and stabilization of liquid foam has been extensively described in the scientific literature (Damodaran 2006; Dickinson 2001; Foegeding and Davis 2011; Lam and Nickerson 2013; Narsimhan and Xiang 2018). Depending on the types of proteins and the presence of other types of surfactants in the foaming system, foam is created and stabilized by following mechanisms.

When only proteins are present in the foaming system

General mechanism of foaming by milk proteins

Immediately after the gas is introduced, the gas-liquid interfacial film is formed and its stability is dependent on the

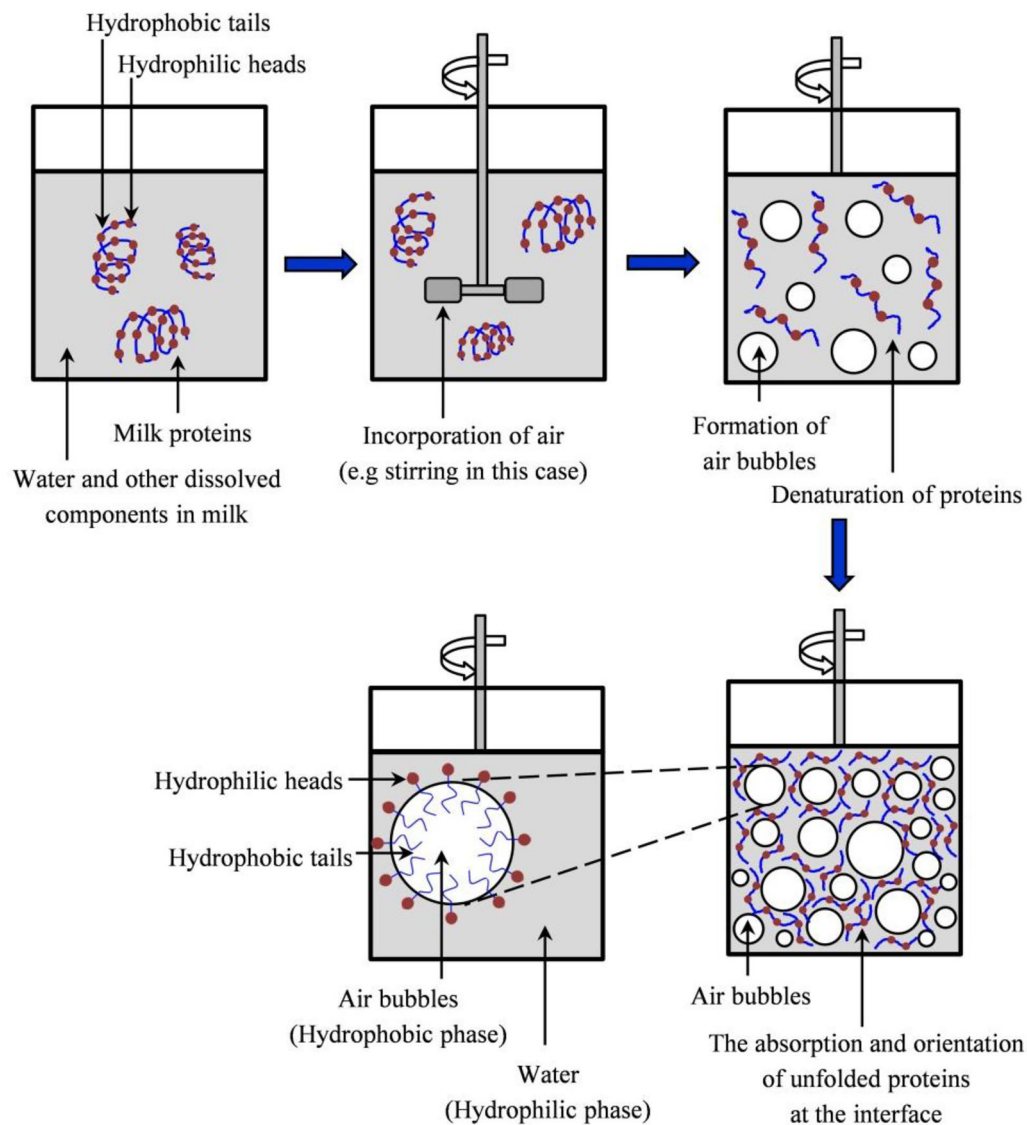


Figure 1. A sketch to illustrate the role of proteins in the formation and stabilization of liquid-based foams.

surface tension between the gas and the liquid. A decrease in surface tension facilitates the formation of the interfacial film, subsequently promoting the formation of the foam (Zayas 1997). In foaming of milk, proteins (caseins or whey proteins) play an important role in the initial formation and subsequent stabilization of the foam. As mentioned, the milk proteins disperse well in water and possess both hydrophilic and hydrophobic groups, and the ability to reorientate these groups at the air-water interface. These properties allow them to diffuse and adsorb rapidly onto the interfacial regions during foaming, leading to a reduction in the surface tension. At the interfacial regions, the proteins unfold and rearrange the polar and nonpolar groups toward the aqueous and non-aqueous phases, respectively. This is followed by the interactions among unfolded proteins primarily by electrostatic and hydrophobic interactions and hydrogen bonds, resulting in the formation of a strong, high viscous and high elastic interfacial film which helps to stabilize the air bubbles (Huppertz 2010; Zayas 1997). The mechanism of this process is demonstrated in Figure 1.

Differences in foaming behavior of caseins and whey proteins

As mentioned, based on their molecular structure, milk proteins can be categorized into flexible (caseins) and rigid/globular proteins (whey proteins). The dissimilarities in the structure of these proteins result in differences in the adsorption rate and surface properties of adsorbed layers, and make them respond differently to factors that drive foaming, such as pH and temperature. Unlike caseins which do not have tertiary structure, whey proteins contain disulfide bridges and possess tertiary structure (Zayas 1997). Thus, at the interfacial films, caseins are ready to change the conformation to take up a larger interfacial area than whey proteins which tend to retain their initial structure (Ipsen and Otte 2004). Moreover, it was found that during foaming of solutions prepared from mixtures of skim milk powder (SMP) and whey protein isolate (WPI), caseins were much more enriched in the foam than the whey proteins (Zhang, Dalgleish, and Goff 2004). In the interfacial regions, caseins are highly susceptible to reversible intermolecular interactions *via* hydrophobic and ionic bonding while whey

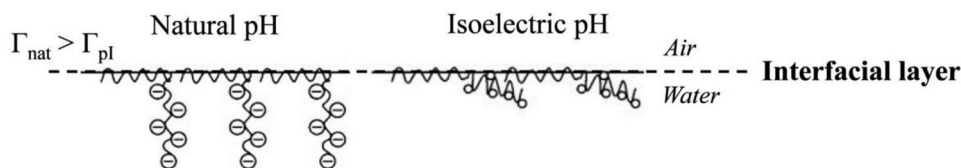
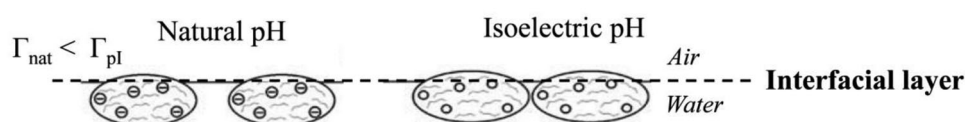
(a): Caseinate (flexible proteins)**(b): Whey proteins (globular proteins)**

Figure 2. An illustration of molecular adsorption of sodium caseinate and whey protein concentrate on the air-liquid interface. Reused with permission from Marinova et al. (2009).

Table 2. Low and high molecular weight surfactants possibly found in milk foaming systems.

Types of surfactants	Foaming properties	Examples
Low molecular weight	Poor	Lipids, phospholipids, lecithin, monoglycerides, diglycerides, and free fatty acids, emulsifiers, sanitizers, cleaning agents
High molecular weight	Good	Proteins

proteins are prone to irreversible polymerization by inter-molecular disulfide bonds (Lee, Morr, and Ha 1992). As a result, the interfacial layer created by caseins is softer and more compressible than that created by whey proteins (Ipsen and Otte 2004).

In order to explain the differences in mechanism of foam stabilization by caseins and whey proteins, Marinova et al. (2009) proposed a model to illustrate the formation of adsorption layers of these proteins as a function of pH, as shown in Figure 2. There was an obvious difference in aggregation behavior of caseins and whey proteins on the interface. For flexible proteins (Figure 2a), at natural pH ≈ 6.5 – 6.8 (far from $pI \approx 4.6$), they formed (1) a dense adsorption layer in a “train”-like configuration (of a thickness of 1–2.5 nm and composed mostly of hydrophobic amino acid residues) adjacent to the interface, and (2) an outer less dense chain (3–7.5 nm) with hydrophilic residues extending into the aqueous phase as a “tail”. At pI , hydrophilic residue chains shrink slightly to the interface and consequently the interfacial adsorption layer becomes denser. This model illustrated that low foamability of caseins at pI is caused not only by casein precipitation, but also by low surface coverage and weak repulsion between the thin film surfaces, which are unable to form and stabilize foam. For globular proteins (Figure 2b), at natural pH, they adsorbed almost intact at the interface. Negative charge and electrostatic repulsion prevented globular proteins from the formation of a dense adsorption layer. At pI (pH ≈ 4.2), slightly positively charged β -lactoglobulin ($pI \approx 5.2$) and slightly negatively charged α -lactalbumin ($pI \approx 4.1$ – 4.8) could interact with each other to strengthen the compaction of the protein molecules at the interface, which leads to stronger interfacial films and better bubble coverage. So, proteins with different structure (e.g. flexible vs globular) exhibit different abilities

to adapt their structural conformation at the interface, and accordingly their foaming properties are different. This is discussed in the following sections.

When proteins and low molecular weight surfactants both are present in the foaming system

In bovine milk, in addition to proteins which can be considered as high molecular weight surfactants with excellent foaming properties, low molecular weight (LMW) surfactants can also be present (Table 2). They either occur naturally in foaming systems such as lipids, phospholipids, lecithin, monoglycerides, diglycerides, and free fatty acids, or are contaminants from processing steps such as cleaning and sanitizing agents (Schramm 2005).

LMW surfactants are relatively small and amphiphilic molecules, thus they diffuse to interfacial regions faster than proteins during foaming. However, they do not have the ability to interact with their neighboring molecules to form a stable interfacial film to stabilize the air bubbles. The differences in molecular structure and properties of LMW surfactants and proteins lead to dissimilarities in the structural properties of adsorbed layers on the air-liquid interface as they stabilize foam *via* different mechanisms (Maldonado-Valderrama et al. 2007; Wilde and Clark 1996). These mechanisms were illustrated by Nylander et al. (2008).

The mechanism of stabilizing air bubbles in the presence of LMW surfactants only, often referred to as “Marangoni effect”. During foaming, LMW surfactants with high mobility adsorb and gather rapidly on the air-liquid interface to form thin films. But, as the LMW surfactant stabilized films are stretched, possibly due to local arrangement of air bubbles under effects of thermal or mechanical perturbations, a local thinning of the films occurs, followed by generation of a surface tension

gradient across the local thinning films, resulting in collapse of the interfacial films. However, if LMW surfactants are present in sufficient amount, thickness and equilibrium surface tension of the thinning films can be restored, against destabilization of air bubbles. They will rapidly and laterally diffuse toward the thinnest region of the films, by which they drag along layers of interlamellar liquid associated with their head groups (Nylander et al. 2008). In contrast, proteins with the ability to interact with each other and to bind with multiple sites on the interfacial regions can form viscoelastic layers. The cohesiveness of adsorbed protein layers and deformability of the adsorbed protein molecules provide the protein stabilized films with resistance against the stretching. The main difference between the foam stabilization mechanisms of low molecular weight surfactants and proteins is the interaction of adsorbed molecules on the surface regions, which is only observed for protein molecules. The incompatibility between the adsorption mechanism of LMW surfactants and proteins at the interfacial region results in instability of thin films, when both of them are present in the foaming system. In such systems, LMW surfactants can compete with proteins for adsorption, coadsorption, or even formation of complexes with proteins on the interfacial films. This interferes with the formation of intermolecular interactions of proteins, resulting in weakening or destroying the integrity, cohesiveness and viscoelastic properties of the interfacial films. Therefore, adding LMW surfactants into protein-stabilized foams will have a detrimental effect on foam stability. In fact, LMW surfactants can be used as anti-foaming agents.

In addition, in a study by Saint-Jalmes et al. (2005), another mechanism of stabilization of foams by proteins (e.g. caseins) and a LMW surfactant (e.g. sodium dodecyl sulfate) was reported. For sodium dodecyl sulfate, the repulsive interactions between the adsorbed surfactant layers allowed to stabilize the thin interfacial film (30-40 nm, initially covered by surfactants) and then foam. For protein, foam was stabilized by the confinement of casein aggregates (which were not previously adsorbed completely on the interface) between air bubbles in the thin films (200-500 nm) via a percolation process. In the mixed protein/surfactant systems, competitive adsorption, and protein-protein and protein-surfactant interactions had significant influence upon their foaming properties, depending on chemistry of the surfactant molecules and surfactant concentration (Maldonado-Valderrama et al. 2007; Wei and Liu 2000). In our recent study (unpublished data), it was found that surfactants, which are different in their electrical charge and molecular weight (Tween 80, sucrose stearate, sodium oleate, sodium dodecyl sulfate, cetyltrimethylammonium bromide, benzalkonium chloride and lecithin), had different effects on foamability, foam stability and foam structure of reconstituted skim milk solutions (8.5%, w/w solid content).

Factors affecting foaming properties of milk

Protein content or solid concentration

Studies on impact of the protein content on the foamability of milk systems vary a lot in their results, however similar

trends have been reported for foam stability which is enhanced at high protein content. Kamath (2007) found that there was a reduction in foamability and an increase in foam stability of reconstituted SMP solution as protein content increased from 0.5 to 5.0% (w/w). Similar effects of increasing protein content (1-3%, w/w) on foaming behavior of whey protein isolate (WPI) and whey protein hydrolysate were also reported (Tamm et al. 2012). The improvement in foam stability at high protein concentration is associated with increasing system viscosity which retards the coalescence of air bubbles, and increasing the protein amount available for formation of high viscoelastic films at the interface. Thus, foams prepared at high protein concentration are more stable and denser. However, an increase in system viscosity at high protein content prevents protein molecules from diffusing to the interfacial regions, by which foamability of milk proteins decreases. In addition, at high protein content, due to fast stabilization of air bubbles during foaming process, which is associated with low foam volume, foaming time required to obtain a certain foam volume increases. However, Martinez-Padilla et al. (2014) stated that an increase in protein content of reconstituted SMP solution (3.6-9.0%, w/w) increased not only its foam stability, but also foamability by approximately 50%, although its viscosity increased by almost 4 times. Similar results were also reported for individual proteins (α -lactalbumin, β -lactoglobulin and casein micelles) and WPI (Dombrowski, Mattejat, and Kulozik 2016). Transition of protein adsorption from diffusion-controlled to adsorption-controlled regime is a possible reason for improvement in foamability at high protein concentrations.

Up to a certain level, an increase in protein content exhibits negative effects on foamability, depending on type of proteins. It was reported that foamability of sodium caseinate and WPI increased steadily with increasing protein content from 0.25 to 4.0 and 8.0% (w/w), respectively, afterwards the foamability of both protein solutions declined sharply (Britten and Lavoie 1992). Similarly, Marinova et al. (2009) reported that protein content corresponding to a plateau value for foamability of sodium caseinate and WPC at neutral pH was 0.3-0.4% and \sim 1.0% (w/w), respectively, and beyond that value there was almost no change in foamability. Foamability dependence on protein content of β -lactoglobulin was almost the same as that on sodium caseinate. Protein concentration at which there was a transition in foamability from an increasing stage to a constant stage was dependent on specific protein properties and foaming conditions (e.g. foaming method and pH). Increasing protein content results in a significant decline in dynamic surface tension which in turn reflects a faster adsorption and better stabilization against coalescence of air bubbles (Marinova et al. 2009).

High protein content affects not only the viscosity of milk, but also the solubility of proteins. A reduction in protein solubility at high concentration results in a decline in foamability. The presence of insoluble particles has a detrimental effect on the foam formation. It was reported that only within the range of concentrations where proteins are

completely soluble, there was a logarithmic relationship between foamability and protein concentration (Britten and Lavoie 1992). While the reported studies have reported comparable results about improvement in foam stability at high protein concentration. Borchering, Lorenzen, and Hoffmann (2009) reported that foam stability of heated skimmed milk was almost unchanged with altering protein content from 1.0 to 6.0% (w/w), although the size of air bubbles in foam significantly decreased with increasing protein content. In order to form one meter square of a monomolecular interfacial layer, only 2–3 mg proteins were sufficient. Higher amount of proteins could lead to the formation of interfacial “loops” and “trains” which result in no effect on foam stability. It can be inferred that the threshold level for changes in foaming properties of milk with an increase in protein concentration is specific for each type of protein and foaming conditions (Marinova et al. 2009). It is worth mentioning that foamability of milk proteins is controlled by adsorption rate which is greatly affected by not only the protein content, but also by protein molecular weight, protein structure and foaming conditions (Martin et al. 2002). Therefore, the research results found in different studies might be not comparable.

Caseins and whey proteins, and their ratios

Due to differences in structure of caseins and whey proteins, the mixtures of these proteins with different ratios show a markedly difference in foaming properties. The presence of proteins with different structures in a foaming system might lead to competitive adsorption at the interface. In a study by Borchering, Lorenzen, and Hoffmann (2009), foaming properties of protein solutions (1.45% protein) with varied casein/whey protein ratios (C/W: 94/6, 80/20, 60/40, 40/60, 20/80 and 7/93) prepared from microfiltrated (casein) and ultrafiltrated (whey protein) retentates were investigated. The results showed that protein solutions with the higher casein proportion produced higher foam volume while those with the higher whey protein proportion produced more stable foam. These results are comparable to findings reported by Martinez-Padilla et al. (2014) on foaming behavior of reconstituted SMP fortified with sodium caseinate and WPC at different C/W ratios. At a similar protein content ($\sim 7.0\%$), foam prepared from the mixtures with $C/W \approx 0.7$ was double in volume, but two times less in half-life as compared to the foam produced from the mixtures with $C/W \approx 9.2$.

By comparing structural and foaming behavior of sodium caseinate and WPI solutions, Lee, Morr, and Ha (1992) found that the higher foamability of sodium caseinate molecules was due to the greater ability to diffuse to the interface, reorient themselves in proper way to reduce surface tension and entrap air while the higher foam stability of WPI was due to the rigid protein film around air bubbles formed *via* intermolecular disulfide bonds. Similarly, Ewert et al. (2016) reported that under similar foaming conditions (e.g. 1.0% protein, pH 7 and 20°C), caseins (e.g. micellar casein concentrate and sodium caseinate) produced a higher

foam overrun than whey proteins (e.g. WPI and WPC80). This is due to the lack of tertiary structure in caseins, resulting in redundancy of the unfolding process at the interface, and subsequently in rapid adsorption at the interface. However, lack of a tertiary or micellar structure in sodium caseinate and high fat content in WPC80 ($\sim 6.5\%$ w/w) made their foams to be much less stable than foams prepared from micellar casein concentrate and WPI, although the air bubble size in micellar casein concentrate foam was larger by 25% than the others. For both caseins and whey proteins, an increase in foaming temperature from 20 to 50°C resulted in a decline of foam overrun and foam stability, except for WPC80 which exhibited an increase in foam stability with increasing foaming temperature. This could be because negative effects of fat are reduced at higher foaming temperatures (Kamath 2007). Nonetheless, in a study by Coppola et al. (2014), it was reported that under similar foaming conditions, foam overrun produced from milk derived WPC containing 22% casein was 2 and 4 times more than that prepared from milk-derived WPC containing 0.9% casein and WPC80, respectively. The foam from milk derived WPC containing 22% casein was also 6 and 18 times more stable than foam from milk derived WPC containing 0.9% casein and WPC80, respectively. The differences in the foaming properties of these systems were caused by not only fat content, but also casein concentration, especially β -casein (which has high molecular flexibility and a high rate of adsorption to the interface) as both WPC samples containing casein were similar in their fat content. These results are contrary to those reported by Dombrowski, Mattejat, and Kulozik (2016). At protein concentration of 1.0% (w/w), β -lactoglobulin exhibited a significantly higher foamability and foam stability than casein micelles. It was explained that the prompt and pronounced intermolecular interaction of proteins at the interface, rather than molecular flexibility of proteins, was a decisive factor for the foamability, while foam stability was dependent on the extent of protein-protein interactions and packing densities of proteins at the air-liquid interface. The lack of intermolecular interactions between individual caseins (e.g. β -casein) was responsible for relatively low foamability and foam stability. A similar foaming behavior was also reported by Martin et al. (2002). At protein concentration of 0.1–3.0% (w/v) and pH 6.7, although molecular size of β -lactoglobulin was smaller than that of β -casein (which is 18 and 24 kDa, respectively), due to self-association to produce a dimer with a higher molecular size and structural rigidity of β -lactoglobulin, it exhibited a slower adsorption rate on the interface and therefore a lower foamability than β -casein. But β -lactoglobulin produced more stable foam than β -casein because of the strong internal structure, low adsorption probability (time to adsorb/attach on the interface) and presence of free disulfide groups which allow a rigid network to be formed on the interface.

The differences in reported results about foaming ability and foam stability of individual proteins indicate that their foaming properties are not only determined by protein properties (e.g. concentration, molecular weight and

structure, and exposed hydrophobic groups), but also by solution conditions (e.g. pH, solvent composition, electrolyte concentrations). Typically, the mixtures with high amount of caseins produced a higher amount of less stable foam than those with high amount of whey proteins.

Size of casein micelles

In milk, caseins exist as aggregates of several thousand individual protein molecules, known as casein micelles. There is a wide range of casein micelle diameter, from < 100 nm to > 300 nm (Dalglish and Corredig 2012). The compositions of casein micelles (α_{s1} -, α_{s2} -, β - and κ -caseins) are dependent on their size. α -Caseins are present throughout the structure of casein micelles, thus they are independent of the casein micelle size, while β -caseins are mostly found in the interior and κ -caseins are predominantly on the surface. Therefore, the smaller casein micelles are higher in κ -casein content and lower in β -casein content (Dalglish and Corredig 2012). Alteration in casein micelle size can be caused by pH (Sinaga, Bansal, and Bhandari 2017), the growth of psychrotrophic bacteria (Burlingame-Frey and Marth 1984), high pressure processing (Hettiarachchi et al. 2018), heating treatment in the presence of whey proteins (Tran Le et al. 2008) and ultrafiltration (Sriakorkul et al. 1991). However, in this review, foaming properties of casein micelles whose size has been altered only by high pressure and ultrafiltration are presented.

Previous studies have shown that foaming properties of milk solutions were greatly affected by the size of casein micelles. Chen et al. (2016) reported that foam stability of casein micelle dispersions prepared by redispersing ultracentrifuged casein micelle pellets at different temperature was strongly related to the size of particles in the dispersions. At the same protein content (e.g. 3%), the half-life value of foam prepared from the dispersion with an average particle size of 500 nm (casein micelles and/or their aggregates) was higher by a factor of six than that of the dispersion with an average particle size of 200 nm (casein micelles). Similarly, Hettiarachchi et al. (2018) found that there was an increase in particle size of the casein micelles in skim milk from ~ 160 nm to ~ 250 nm as the milk was subjected to high pressure processing at ≥ 300 MPa, which affected its foaming properties. Foam expansion index was reported to be more than 100% for samples processed at pressures ≥ 300 MPa and it was attributed to rearrangements in casein micelle morphology. Under effects of temperature and extreme shearing forces at high pressure, casein micelles could have dissociated into casein monomers or particles, followed by their rearrangement into amorphous large casein aggregates. During foaming process, casein monomers or particles could have released faster from the casein aggregates than from intact micelles, resulting in rapid migration and adsorption at the interface which markedly enhanced foamability and foam stability. In addition, increase in viscosity associated with the formation of large casein aggregates is also responsible for improving foam stability. Mac (2014) studied the foaming properties of casein micelle suspensions (0.1%

protein) containing casein micelles with average size of 64, 116, 156 and 194 nm prepared by successive centrifugation of whole casein micelles. Their results showed that a decrease in casein micelle size slightly enhanced the foaming capacity, but drastically improved the foam stability as there was an increase in the half-life values from 9 min to 74 min for casein micelle size from 194 to 64 nm. The larger casein micelles had lower foaming capacities since their diffusion and adsorption at the interface might be slower than that of the smaller ones. In addition, there was a marked change in casein micelle composition with a decrease in micelle size. An increase in casein micelle diameter from 64 to 194 nm led to a decrease in κ -casein content, from 25.6 to 20.3%, and an increase in β -casein content, from 30.7 to 44.5%, while α_s -caseins remained unchanged ($\sim 45\%$). It seems that effect of casein micelle size on foaming properties is determined by the method used to induce size alteration, which can affect integrity and structure of casein micelles, and composition of casein micelles.

Presence of low molecular weight surfactants

LMW surfactants present naturally in milk include fat and its degradation products. In foaming of milk proteins, the presence of these compounds, even at a very small amount, leads to detrimental effects on the formation and stabilization of the foam. The differences in the adsorption mechanisms at the interfacial region between them and protein molecules, which counteract each other, result in the rupturing of the interfacial film of foam (Nylander et al. 2008). In milk, fat exists in the form of emulsified globules (2–4 μ m in diameter) coated with a membrane mainly made of phospholipids, cholesterol, lipoproteins, glycoproteins and proteins (Kontkanen et al. 2011). Concentration and composition of milk fat is dependent on season and geographic location, particularly on climate variation, stage of lactation, farming practices, pasture availability and supplementary feed inputs (Chen, Lewis, and Grandison 2014; Liu et al. 2017). Any damage to the fat globule membrane possibly caused by physical actions during processing (such as cooling, agitation, mixing, homogenization and freezing/thawing), allows lipase enzymes to access the milk fat by which lipolysis is initiated and as a result triglycerides are broken down into diglycerides, monoglycerides and free fatty acids (FFA). It has been reported that FFA is present in milk in a small quantity as a result of incomplete synthesis of triglycerides (Deeth 2006), and its increase in concentration was dependent on herd production system, milking system, feeding and technological factors (Wiking et al. 2019).

Many studies have reported that milk with a high fat content exhibits very poor foaming ability and stability as compared to ones with a low fat level, and that skim milk, even reconstituted skim milk powders, create stronger and more stable foams than whole or full-cream milk (Anderson and Brooker 1988; Goh, Kravchuk, and Deeth 2009; Huppertz 2010; Walstra 1989). Apart from the extremely low fat content, skim milk, especially skim milk powders,

also contain a high amount of lactose which has a great water holding capacity. This property of lactose contributes to an increase in the viscosity of milk by which the stability of adsorbed protein films is markedly enhanced (Gamboa and Barraquio 2013). The destructive effects of milk fat on the foaming properties of milks have been reported. The foamability of milk containing less than 0.04% (w/w) fat was nearly double compared to that of milk containing 1.5 and 3.0–3.9% fat (w/w) (Gamboa and Barraquio 2013). Similarly, Anderson and Brooker (1988) reported that the foamability of milk significantly decreased with an increase in the fat concentration from 0 to 1.5%. Goh, Kravchuk, and Deeth (2009) stated that regardless of the foaming method (e.g. mechanical agitation, steam injection and air bubbling) and heat treatment approaches (pasteurization and ultra-high temperature treatment), the foams obtained from skim milk were significantly stronger and lasted longer than those prepared from full-cream milk.

The influence of fat level on the foaming properties of milk is dependent on the temperature at which the foam is created because the temperature affects the physical state of the milk fat. The heterogeneity and complexity in the structure and the degree of saturation provide milk fat with a very wide range of melting temperate, ranging from -40 to $+40^{\circ}\text{C}$. Thus, at temperature less than 40°C , the milk fat globules contain a mixture of liquid fat and solid fat existing as crystals. During foaming under mechanical forces, the solid fat crystals with sharp edges and corners can pierce the membrane of fat globules, resulting in the deformation of milk fat globules and the spreading of the membrane materials and liquid fat over the liquid films of the air bubbles. This spreading leads to the disruption of foam lamella and coalescence of air bubbles because the liquid fat is unable to form viscoelastic interfacial film to stabilize the foam, although it is readily adsorbed on the air-liquid interface due to its high mobility (Walstra et al. 1999). Therefore, the negative effects of milk fat on the foaming become more predominantly evident as the foaming process is performed at temperature less than 40°C , especially in the range of 10 – 40°C . Kamath, Huppertz, et al. (2008) reported that at a temperature range of 5 – 45°C , there was a large difference in foamability and foam stability between skim and whole milk in which the former showed a significantly higher foaming capacity and foam stability than the latter. Nevertheless, as the foaming temperatures were higher than 45°C , a similarity in the foamability between them was observed, and other factors such as heat treatment and homogenization, rather than fat content had a major effect on the foam stability. This is because at temperatures higher than 40°C , milk fat globules contain only liquid fat, which is far less influential on the deformation of the foam lamella. At temperatures less than 10°C , the milk fat globules are predominantly occupied by the solid fat. This provides the milk fat globules with a markedly higher resistance to the deformation, thus the foamability of milk is less effected at those temperatures (Huppertz 2010). However, at the whole range of foaming temperatures (5 – 85°C), the foam produced from skim milk still is much more stable than that prepared from the whole

milk. The reasons possibly are that regardless of the physical state of milk fat (liquid or solid fat), it is unable to contribute to the formation of stable interfacial films as proteins do. Similar findings were also reported by Pilhofer et al. (1994) in which the creation and stabilization of milk foam were highly dependent on the fractions of the milk fat. In conclusion, for both whole and skim milk, it is better to perform the foaming process at high temperature (50 – 60°C) at which milk fat, containing only liquid fat, has less influence on the development and stability of foam (Borcherding, Hoffmann, et al. 2008; Kamath, Huppertz, et al. 2008). Moreover, the milk fat also affects the appearance and size distribution of air bubbles. It was reported by Kamath, Huppertz, et al. (2008) that the foam prepared from whole milk was smaller in size and narrower in size distribution than the foam prepared from skim milk. A higher viscosity of whole milk enhances the formation of smaller bubble size and prevents air bubbles from coalescence. However, the air bubbles in the foam prepared from whole milk ruptured at a markedly higher rate.

In addition, the particle size of milk fat globules greatly affects the formation and stabilization of foam, especially for those prepared from whole milk at high temperatures. It was reported that at temperature under 40°C , both unhomogenized and homogenized whole milk were unable to form the foam which can last for several minutes. At higher than 40°C temperatures, a size reduction of the milk fat globules accomplished by homogenization improved the foam stability of whole milk three to four times, but almost did not significantly affect the foamability (Kamath, Huppertz, et al. 2008). This increase in foam stability could be due to several reasons. Firstly, after homogenization, the solid fat crystals become too small to disrupt the foam lamella. In addition, the homogenization substantially increases the surface area and the number of the fat globules. This results in a deficiency of the milk fat globule membrane material and liquid fat available to stabilize the newly generated surface of homogenized fat globules. Thus, the amount of liquid fat released from the homogenized fat globules can be insufficient to cause the thinning of liquid films. Moreover, as there is a shortage of membrane material of fat globules, the newly formed surface of the homogenized ones is reinforced by casein micelles and whey proteins, making it much more resistant to disruption as compared to the natural fat globule membrane (Huppertz 2010; Truong et al. 2016). Similarly, Borcherding, Hoffmann, et al. (2008) reported that whole milk with 3% fat (w/w), homogenized by a two-stage homogenization at 200 bar (first stage) and 50 bar (second stage), exhibited a very poor foamability and foam stability when the foaming process was performed at low temperatures, especially at 20°C at which milk fat globules contained about 20% (w/w) solid fat crystals which were apparently detrimental to the foaming process. However, the whole milk which was homogenized under similar conditions had only marginal effect on the formation and stability of foam when the foaming process was performed at 50°C , at which the fat globules contained only liquid fat. These research results

demonstrate that the physical state of milk fat in terms of the ratio of solid and liquid fat affected by the foaming temperature is more important than the size reduction of milk fat globules accomplished by homogenization in determination of the creation and stabilization of foam produced from whole milk.

As milk fat globules were in native state ($D[4,3] = 0.8, 2.6, 3.7, 4.7$ and $5.5 \mu\text{m}$), which were obtained by using a modified commercial cream separator along with varying of operating conditions, foamability of the milk samples only improved when the size of milk fat globules was smaller than $2.6 \mu\text{m}$ while the foam stability was not affected by the size (Ho et al. 2021).

Similar negative effects of residual lipids on the foaming properties (capacity and stability) of whey protein concentrates have been reported (Karleskind et al. 1995; Kim et al. 1989; Patel and Kilara 1990; Peltonen-Shalaby and Mangino 1986; Rinn et al. 1990; Vaghela and Kilara 1996). In these studies, it was reported that the whey protein concentrates with a higher lipid content display a poorer foaming capacity and a lower foam stability than those with a lower lipid content. Moreover, it was reported that the hydrolysis of phospholipids by lipase from *Mucor miehei* or *Fusarium venenatum* phospholipase A1 showed a significant improvement in the formation and stability of the foam generated from both milk and whey protein concentrates (Blecker et al. 1997; Lilbaek et al. 2007).

The effect of lipolyzed products on frothing ability of milk was firstly reported by Buchanan (1965). It was stated that monoglycerides and diglycerides, not FFAs, had a strong detrimental effect on the foamability of milk. Moreover, an addition of a mixture of commercial monoglycerides and diglycerides into milk also showed a similar depressing effect on the foamability to that caused by those produced from lipolyzed milk. In subsequent studies (Deeth and Smith 1983; Kamath, Wulandewi, and Deeth 2008; Kitchen and Cranston 1969), it was found that the formation and stabilization of foam substantially reduced with an increase in FFA content. (Deeth and Smith 1983) reported that an increase in FFA from about 0.8 to $1.2 \mu\text{equiv/mL}$ led to a decrease of about 60% frothing value. At concentrations higher than $2.0 \mu\text{equiv/mL}$, the frothing ability of milk was negligible. Also, mixing of a lipolyzed milk ($3.5 \mu\text{equiv/mL}$ of FFA) with an unlipolyzed one ($< 0.75 \mu\text{equiv/mL}$ of FFA) significantly decreased the foamability of the latter. Thus, on a milk farm, mixing of several types of milk, in which at least one has been lipolyzed, into a tanker can cause foaming problems for the whole bulk of the milk. Similarly, Kamath, Wulandewi, and Deeth (2008) illustrated the depressing effects of FFA on the foamability and stability of foam (Figure 3). However, the starting point of FFA level inducing the negative effect on foaming ability was different from those reported by Deeth and Smith (1983). High volume of stable foam was still obtained at the FFA levels higher than $2.0 \mu\text{equiv/mL}$ although the same foaming method (steam injection at $65\text{--}70^\circ\text{C}$) was employed (Figures 3a and b). The differences in the results of two studies are possibly explained by the dissimilarities in heat treatment

and homogenization conditions of milk prior to foaming, both of which affect the particle size of fat globules and the integrity of proteins, and in the methods used to induce the lipolysis of milk fat. In our recent study (unpublished work), we confirmed that the different ways to induce lipolysis in milk had different effects on foaming properties. Unlike ultra-turrax-induced lipolysis which caused the foaming ability of milk to drop rapidly as FFA content was higher than $2 \mu\text{equiv/mL}$, microfluidised-induced lipolysis led to a steady decrease in the foaming ability of milk with a correlation coefficient of 0.9 (Figure 3d).

As displayed in Figure 3c, FFA content also affected the appearance of foam in which a foam with smooth and creamy texture was only obtained at low FFA content and an increase in FFA concentration resulted in an increase in foam coarseness. In addition, it was also reported that in air aeration foaming method, the depressing effect of FFA on foaming stability was dependent on temperature at which foam was produced. At $< 3.0 \mu\text{equiv/mL}$, the negative effects of FFA on the foam stability at low foaming temperature (e.g. 5°C) was more profound than at high foaming temperature (e.g. 65°C), while at $> 3.0 \mu\text{equiv/mL}$, the adverse effect of FFA was irrespective of the foaming temperature. A rapid absorption ability of proteins at high temperature, making them more effective in competing with FFA to adsorb on air-liquid interface, resulted in a higher foam stability at high foaming temperature than that at low foaming temperature (Kamath, Wulandewi, and Deeth 2008).

Furthermore, it was found that addition of refined oils (e.g. olive oil, sunflower oil and canola oil) into reconstituted SMP declined its foamability, but increased foam stability due to an increase in viscosity of milk with added oils (Kamath 2007). The effects of added oils on foaming properties were primarily decided by oil concentration, not by type of oil and foaming method. Moreover, because refined oils are fully liquid at temperatures higher than 0°C and substances such as phospholipids, monoglycerides, diglycerides and FFAs, which have destructive effects on the foaming properties, are removed during refining process, the foamability and foam stability of milks added with refined oils were significantly higher than those of milk contained milk fat at the same concentrations (Kamath 2007).

pH

Typically, pH of fresh raw milk under normal conditions is approximately 6.5–6.6, and any changes in pH result in changing the charge, structure (flexibility), surface activity, ionic strength, and intra- and intermolecular interaction ability of proteins (Ward et al. 1997) as well as dissociation rate of minerals and caseins (Broyard and Gaucheron 2015). All of these alterations in turn affect the availability of surface active substances, rheological properties of interfacial films and milk viscosity, and subsequently foaming behavior. A summary on reported studies on effect of pH on foamability and foam stability of milk and milk proteins is shown in Table 3. It was reported that starting at the neutral pH

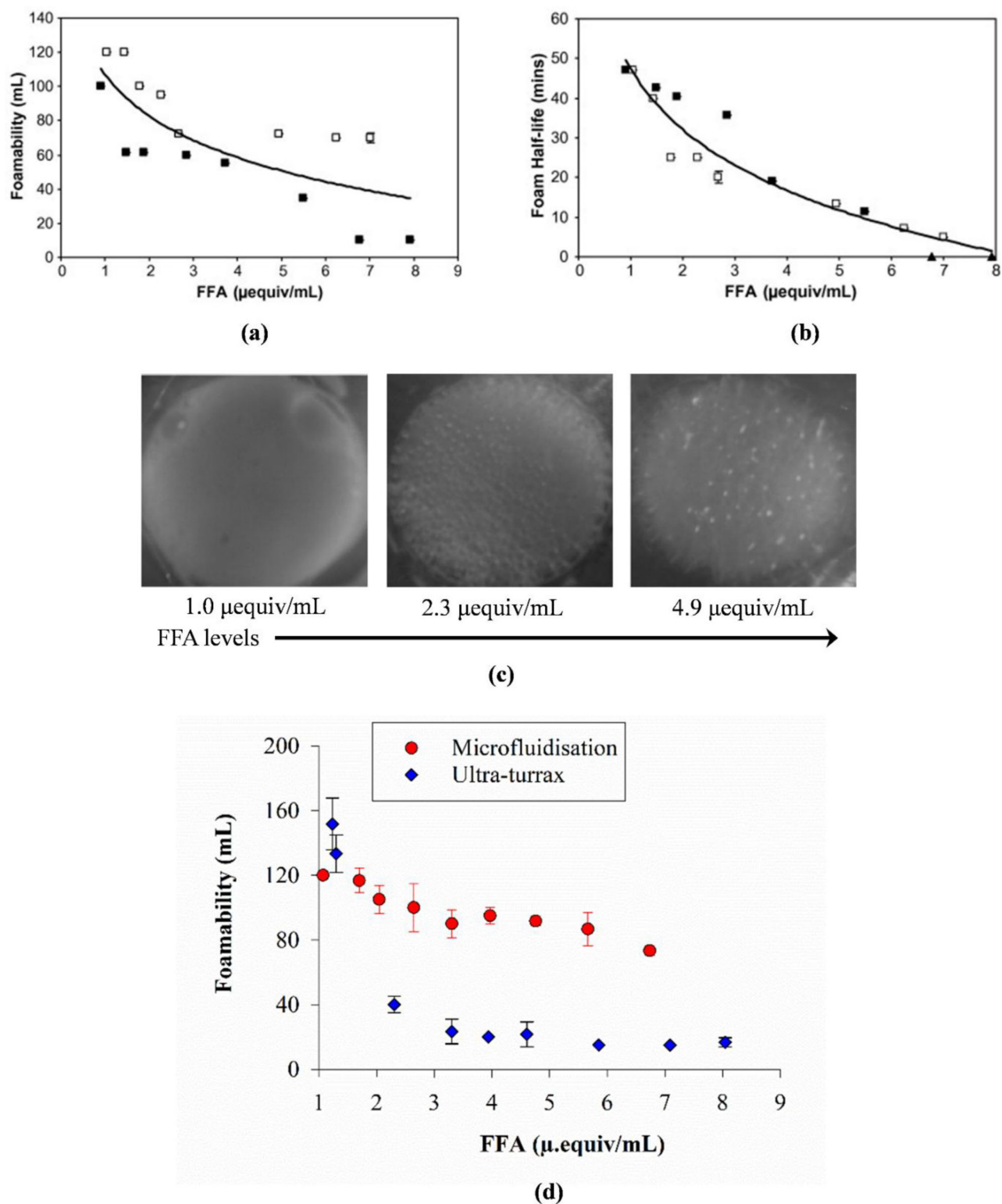


Figure 3. Relationship between FFA content and foamability (a), foam stability (b), appearance of foam (c), and differences in foaming ability of milk in which FFA has been produced by microfluidisation and ultra-turrax (d). The images were taken soon after steam injection (65–70°C) was stopped. (■) Lot I, (□) Lot II of milk employed for studying. Adapted with permission from Kamath, Wulandewi, and Deeth et al. (2008).

(~ 6.6) of reconstituted SMP solution (9.6%, w/w), both lowering the pH to 5.5 and increasing the pH to 7.7 markedly enhanced foamability and foam stability. Improving foamability associated with a pH reduction is a result of increase in extent of dissociation of minerals and caseins from casein micelles, leading to more proteins available to

adsorb on the interface. In addition, lowering the pH reduces the protein charge, promoting the intermolecular interactions on the interface and then foam stability. Meanwhile, the enhancement of foaming properties at pH higher than 6.5 ($\text{pH} \approx 6.5\text{--}7.7$) is generally due to an increase in casein solubilization and viscosity (Augustin and

Table 3: A summary on reported studies on effect of pH on foamability and foam stability of milk and milk proteins.

Samples	Solid concentration (%)	pH	Foamability	Foam stability	References
RSMP	9.60	6.6 → 5.5	Markedly improved	Markedly improved	Augustin and
		6.6 → 7.7	Slightly improved	Significantly improved	Clarke (2008)
RSMP	10.00	6.6 → 6.0	Slightly improved	Slightly improved	Ward et al. (1997)
		6.6 → 7.8	Markedly improved	Significantly improved	
RSMP	1.40	3.0 → 8.0	<ul style="list-style-type: none"> • Highest at pH 3.0 • Lowest at pH 4.5 • Markedly improved at pH 4.5-8.0 	Not determined	Zhang et al. (2004)
WPI	0.55	3.0 → 8.0	Highest at pH 4.0-4.5 Lowest at pH 3.0		
Skimmed milk	No reported	6.4 → 7.0	Improved	<ul style="list-style-type: none"> • Comparable • Highest at pH 6.7 	Borcherding et al. (2009)
Sodium caseinate	0.10	3.0 → 6.8	<ul style="list-style-type: none"> • Lowest at pH 4.6 • Markedly increased from pH 4.6 to 3 and 4.6 to 6.8 	<ul style="list-style-type: none"> • Lowest at pH 5.0 • Highest at pH 6.8 	Marinova et al. (2009)
WPC	0.10	3.0 → 6.8	<ul style="list-style-type: none"> • Highest at pH 4.2 • Markedly declined from pH 4.2 to 3 and 4.2 to 6.8 	<ul style="list-style-type: none"> • Highest at pH 4.0-4.5 • Declined beyond pH 4.0-4.5 	
WPI	5.00	4.0, 5.0, 7.0	<ul style="list-style-type: none"> • Highest at pH 5.0 • Lowest at pH 4.0 	<ul style="list-style-type: none"> • Highest at pH 5.0 • Lowest at pH 4.0 	Phillips et al. (1990)
Casein micelles	10.00	6.0 → 11.0	Significantly and steadily increased	<ul style="list-style-type: none"> • Lowest at pH 6.0 • Highest at pH 9.0 • Markedly declined at pH 10 and 11. 	(Dombrowski et al., 2016)

Where, RSMP = reconstituted skim milk powder

WPI = Whey protein isolate

WPC = Whey protein concentrate

Clarke 2008). Similar results were also reported by Ward et al. (1997) on reconstituted SMP solutions (10%, w/v) within a pH range of 6.0-7.8. However, Zhang, Dalgleish, and Goff (2004) reported different results about effect of pH on foamability of reconstituted SMP solution (1.4%, w/w, corresponding to 0.5% protein). Its foamability was highest at pH 3.0, lowest at pH 4.5 (e.g. six times less than at pH 3.0), and increased steadily from pH 4.5 to 8.0. A poor foaming between pH 4.0-4.5 is due to the precipitation of caseins, but decreasing the pH to 3.0, which is far below isoelectric point, allows resolubilisation of caseins to occur, by which foamability is recovered and reaches to a maximal value. The dephosphorylation of caseins is possibly responsible for increase in foamability at alkaline pH (Zhang, Dalgleish, and Goff 2004).

Because of the differences in structure and properties of individual proteins, the effect of pH on their foaming properties varies. For skimmed milk, increasing pH from 6.4 to 7.0 caused increased foamability and average air bubble diameter, while foam drainage was widely comparable, with a minimum value at pH 6.7. SDS-PAGE results indicated that the highest stability of foam prepared at pH 6.7 was possibly due to highest amount of β -caseins adsorbed on the interface (Borcherding, Lorenzen, and Hoffmann 2009). For sodium caseinate (0.1% w/w), the foamability was lowest at pH 4.5, and markedly increased with lowering the pH to 3.0 and increasing the pH to 6.8 where foam stability was highest (Marinova et al. 2009). In contrast, foaming properties of WPI and WPC were opposite to those of reconstituted SMP solutions and skimmed milk. It was reported that the foaming of WPI (0.55%, w/w) was highest at pH 4.5, lowest at pH 3.0, and markedly dropped at alkaline pH (\approx 4.5-8.0) (Zhang, Dalgleish, and Goff 2004). Likewise, it was also

found that between pH 4.0, 5.0 and 7.0, both foam ability and stability of WPI (5%, w/w) were highest at pH 5.0 and lowest at pH 4.0 (Phillips, Schulman, and Kinsella 1990). Similar to WPI, the foaming capacity of WPC (0.1% w/w) was highest at low pH (pH \approx 4.2) and the foam was very stable, while at neutral pH (pH \approx 6.8), WPC produced markedly less and unstable foam (Marinova et al. 2009). For casein micelles (10%, w/v), alkalisation from pH 6.0 to 11 led to a significant effect on their size, structure and composition. Due to this their foamability steadily improved while foam stability was lowest at pH 6.0, markedly increased up to pH 9.0 and then sharply declined at pH 10 and 11 (Dombrowski, Dechau, and Kulozik 2016). The differences in the foaming properties of milk proteins at different pH levels are related to their structure, their competitive adsorption on the air-liquid films, and degree of protein-protein interactions, which respond differently to pH alteration. However, the effect of pH on foaming properties of milk proteins are also dependent on other processing factors such as heat treatment, addition of additives (e.g. calcium chelating agents and NaCl) or protein concentration.

Temperature

Foaming temperature

Influence of foaming temperature on foaming behavior of whole and skim milk is very different because the foaming temperature affects the physical state of fat globules present in whole milk. For whole milk, it was reported that foamability sharply decreased within a temperature range of 5-35 °C and progressively increased with an increase in temperature from 45 to 85 °C. Similarly, stability of foam produced from whole milk at temperatures lower than 40 °C

was negligible, but was significantly enhanced at temperatures higher than 40 °C, especially for foam produced from whole milk initially subjected to homogenization and heat treatment. In contrast, foamability of skim milk continuously increased with an increase in temperature from 5 to 85 °C while foam stability was highest at 45 °C and both lowering and increasing the temperature resulted in a marked reduction in foam stability (Kamath, Huppertz, et al. 2008). Similar results about the effect of different temperatures (4–60 °C) on foaming properties of whole and skim milk were also reported by Borcherting, Hoffmann, et al. (2008) and Borcherting, Lorenzen, et al. (2008). For both whole and skim milk, foam produced at temperatures of 40–60 °C was much higher in capacity and stability than that produced at temperatures lower than 40 °C. Similarly, for milk based espresso coffees, an increase in foaming temperature from 50 to 70 °C enhanced both foam capacity and stability (Khezri, Shahriari, and Shahsavani 2017). In another study on effects of temperature on the foaming properties of ultra-high temperature treated and pasteurized milk, each containing 1.5 and 3.5% (w/w) fat, it was shown that foaming behavior of all types of milk showed a similar trend in response to an increase in foaming temperature. Foam ability and stability of all types of milk were lowest at 25 °C. Both reducing foaming temperature from 25 to 5 °C and increasing from 25 to 60 °C displayed a strong increase in foam ability and stability, with a markedly larger extent observed for the latter case (Oetjen et al. 2014).

In addition, foaming temperature also affects size and homogeneity of air bubbles. A higher foaming temperature resulted in smaller size of air bubbles (Borcherting, Lorenzen, et al. 2008). The effects of foaming temperature on foaming properties of milk can be explained by several factors. At temperatures lower than 40 °C, the existence of solid fat crystals in the fat globules has detrimental effects on foam ability and stability (Kamath, Huppertz, et al. 2008). Thus, a poor foaming capacity and low foam stability is often observed at 25–35 °C. Foaming at high temperatures results in a decrease in apparent viscosity of milk and surface tension of proteins, enhancing the adsorption rate of proteins to interfacial regions. Moreover, the number of hydrophobic interactions on the interface increases at elevated temperatures due to exposure of hydrophobic groups (which might be hidden at low temperature) and reduction of protein net charge (electrostatic repulsion) as a result of slight decrease in pH at high temperature (Borcherting, Lorenzen, et al. 2008). However, foaming at very high temperature (> 65 °C) causes a significantly drop in foam stability (Kamath, Huppertz, et al. 2008). It is possibly because of over denaturation of proteins, especially whey proteins, resulting in a reduction of strength and viscoelasticity of interfacial protein layers. Due to their poor thermal stability, at temperatures higher than 60 °C, whey proteins could be denatured and form polymers with itself or with caseins (Qian et al. 2017).

Heat treatment of milk prior to foaming

Depending on heating conditions, milk proteins undergo many changes in casein micelle size, dissociation of casein

from micelles, denaturation of proteins, degree of protein interactions and aggregation, even pH and viscosity of milk (Considine et al. 2007; Elliott et al. 2005; Qi et al. 2015; Raikos 2010). All these changes greatly impact the molecular structure and functionality of milk proteins and, thus, the foaming properties of heated milk are greatly affected. About a review of effects of heating on the interfacial properties of milk proteins has been published by Raikos (2010). It was reported that pretreatment of skim milk by high temperature short time (HTST, 75 °C/16s, high temperature (90–120 °C/20s), and ultra-high temperature (UHT, 140 °C/5–10s) strongly reduced foam density possibly because of increased exposure of functional groups caused by heat-induced partial unfolding of whey proteins. The denaturation of whey proteins altered the surface rheological properties, by which the stability of foam significantly reduced with an increasing heat input. Thus, the most stable foam was obtained from unheated milk whereas the least stable one was observed for UHT milk (Borcherting, Lorenzen, et al. 2008). The findings are comparable to those reported by Kamath, Huppertz, et al. (2008). At different foaming temperatures (5–85 °C), HTST- and UHT-treated skim milk did not exhibit a significant difference in foamability, but foam produced from HTST-treated milk was much more stable than UHT-treated skim milk foam. However, an opposite trend was observed for homogenized whole milk. As compared to HTST-treated whole milk, the UHT counterpart had a higher foamability (especially at foaming temperatures of 5–35 °C) and produced more stable foam. A high degree of association of whey proteins with caseins on the surface of the homogenized milk fat globules and a high viscosity in response to the extent of heating results in a better foamability and a higher foam stability of UHT homogenized whole milk (Kamath, Huppertz, et al. 2008).

Moreover, heat treatment conditions prior to the production of SMP powder also altered its foaming behavior. It was reported that high-heat-treated SMP (85 °C/30 min) exhibited a markedly higher foam ability and stability than low-heat-treated SMP (72 °C/30s) (Augustin and Clarke 2008). For WPI, effects of heating at 25, 55 and 80 °C on foaming properties were dependent on pH. At pH 4.0 and 5.0, an increase in heating temperature (25–80 °C) drastically declined overrun; but at pH 7.0, the overrun was only improved at 25 and 55 °C, and a further increase to 80 °C highly impaired foamability. Heat treatment had almost no effect on foam stability at pH 4.0 and 7.0 while at pH 5.0 heating at 80 °C improved foam stability by 65% as compared to the other temperatures (Phillips, Schulman, and Kinsella 1990). Besides heating temperature, heating time also affects foaming behavior of WPI. It was found that at pH 7.0, WPI heated at 70 °C/1 min displayed a better foamability and foam stability than either the unheated WPI, or WPI heated at 70 °C for longer time and at 90 °C/1–90 min (Zhu and Damodaran 1994b). Similarly, it was reported that heat treatment at 85 °C/3 min increased foamability and foam stability to highest values and prolonging the heating time more than 3 min was detrimental to foaming properties (Moro et al. 2011). These findings indicate that foaming

behavior of WPI was greatly influenced by degree of denaturation of β -lactoglobulin (main component in WPI). Bals and Kulozik (2003) reported that foaming ability, foam stability and foam rigidity of WPI were improved as degree of denaturation of β -lactoglobulin was less than 76%. At higher degree of denaturation, all these foam characteristics were declined. It seems that a good foaming ability and high stability of the foam are associated with a heterogeneous proportion of native, unfolding and denatured proteins.

Homogenization

In milk processing, the primary purpose of homogenization is to reduce particle size of fat globules to prevent creaming process. Thus, this process is typically accomplished at pressure less than 100 MPa and applied to whole or full cream milk. It was reported that homogenization of whole milk at pressure of 6.9–20.6 MPa markedly increased steam frothing value (Deeth and Smith 1983). However, at different foaming temperatures, the effects of homogenization on foaming behavior are different. At foaming temperature of 5–40 °C, raw whole milk exhibited a significantly lower foamability than homogenized whole milk, but at foaming temperature higher than 40 °C there were no noticeable difference in their foamability (Kamath, Huppertz, et al. 2008). There are several reasons for the improvement in foaming behavior by homogenization. Firstly, homogenization causes a substantial increase in the surface area and the number of fat globules, resulting in an insufficiency of the amount of liquid fat released from fat globules to cause the thinning of liquid films. The increase in the number of fat globules leads to a deficiency in membrane material available to stabilize the newly generated surface of homogenized fat globules. In this case, the newly formed surface is reinforced by casein micelles and whey proteins, as a result of which a substantial increase in its resistance to disruption is attained as compared to natural fat globule membrane. Moreover, homogenization probably makes the solid fat crystals in the fat globules too small to disrupt the foam lamella (Huppertz 2010). At temperatures higher than 40 °C, milk viscosity is reduced and the fat globules contains only liquid fat, therefore homogenization did not show a markedly improvement in foamability of whole milk as foaming process is accomplished at temperatures higher than 40 °C. In contrast, foam stability exhibits an opposite trend. At temperatures lower than 40 °C, it was impossible to form foams lasting for a few minutes from both raw and homogenized whole milk. However, at temperatures higher than 40 °C, the size reduction in fat globules by homogenization improved the foam stability of whole milk by almost fourfold (Kamath, Huppertz, et al. 2008). Moreover, Borchert, Hoffmann, et al. (2008) reported that when foam was produced at 50 °C, the two-stage homogenization with a pressure of 5–25 MPa in the first stage and 5 MPa at the second stage almost did not have a major effect on the foamability and foam stability of whole milk although particle size of the fat globules was reduced by about 10 times. From the results of these studies, it can be inferred that homogenization only

affects the foaming behavior of whole milk when foaming is performed at low temperature (< 40 °C) where the milk fat globules contain a significant amount of solid fat crystals.

Homogenization of milk at extremely high pressure (> 100 MPa), known as microfluidization, exhibits a different tendency for changes in foaming properties of milk. It was reported that an increase in microfluidization pressure of pasteurized whole milk from 125 MPa to 500 MPa led to an increase in foamability by 85% although apparent particle size of milk was decreased by 10 times and viscosity was increased by two folds. For stability, foam prepared from the control totally collapsed within an hour while half-life value for foam produced from the milk processed at 500 MPa was about five hours (Tran et al. 2018). The results of this study suggest that the dissociation of casein micelles into surface active casein proteins and the formation of casein-fat complexes during microfluidization at high pressure were associated with changes in foaming properties.

Foaming methods

Comparing foam stability generated by steam injection, air bubbling and mechanical agitation, Goh, Kravchuk, and Deeth (2009) found that the stability of full-cream milk foam was similar amongst three foaming methods while skim milk foam generated by mechanical agitation was significantly more stable than that created by the other two approaches. For foam strength, there were markedly differences among these foaming methods in which steam injection created the strongest foam and air bubbling generated the weakest foam. The foam created by various foaming methods exhibited different properties due to dissimilarities in the manner of incorporating air into the bulk liquid of the milk and the foaming conditions (e.g. foaming temperature and time) which greatly affect viscosity of liquid milk and functionality of milk components (e.g. physical state of milk fat, adsorption kinetic of surface active substances and denaturation extent of proteins). Thus, mechanism of formation and stabilization of interfacial layer of foam by different foaming methods is different. The dissimilarities in the properties of foam prepared *via* mechanical agitation and steam injection under a particular foaming condition were reported (Augustin and Clarke 2008; Ho et al. 2019; Silva et al. 2008). Addition of citrate (0.1–0.5 mol/kg serum solid) into reconstituted SMP solution (10%, w/w) significantly improved the whipping-frothing properties in terms of foamability and foam stability, but did not enhance any steam-frothing properties (Augustin and Clarke 2008). Differences in the properties of foam produced by steam injection and whipping methods were also reported by Silva et al. (2008). However, effects of foaming methods were also dependent on types of milk. It was found that for raw whole milk at the same foaming temperature (65 °C), mechanical mixing foaming method exhibited a much lower foamability as compared to air and steam injection counterparts. However, for raw skim milk and pasteurized whole and skim milk, foamability of these methods were similar (Ho et al. 2019). Moreover, in a foaming approach, for example

steam injection, the changes in process parameters, such as steam pressure and nozzle design, led to differences in foamability, foam stability, and even size of air bubbles and texture (Jimenez-Junca et al. 2015). The results of these studies suggest that foaming method has a great impact on the foam properties and that a lack of a common method of foaming could lead to differences in results from various studies.

Aging of milk

There is a widely-accepted notion that aged milk gives much higher foam quality than fresh milk and many manufacturers of foaming equipment recommend to age milk at 4 °C for at least 24 h to improve foaming properties of milk. However, findings of many studies do not support this notion. It was reported that storage of milk at 4 °C for 3 days did not significantly affect the steam frothing ability (Deeth and Smith 1983), but slightly declined tit and increased the percentage of foam dissipation after 10 days of storage (Levy 2003). However, Gamboa and Barraquio (2012) found that aging milk at 4–11 °C for 9 days resulted in a significant decrease in foamability, but did not affect the percentage of foam dissipation. The changes in foaming properties of milk during aging are possibly caused by proteolysis and lipolysis of milk. The net effect of these processes (proteolysis and lipolysis) lead to different effects of aging on foaming properties. Thus, storage at 4 °C for 15 days increased the steam frothing value of skim milk, but almost did not affect the steam frothing value of whole milk (Nanua et al. 2004). In case of milk powder, it was reported that the changes in physicochemical and biochemical properties (e.g. lactose crystallization, fat migration and powder aggregation) during storage dramatically decreased solubility and structural flexibility of proteins, resulting in a decline in the foaming properties of milk powders (Thomas et al. 2004). In a recent study on foaming properties of raw whole, raw skim, pasteurized whole, and pasteurized skim milk during storage at 4 °C (Ho et al. 2019), it was reported that although there was a slight increase in free fatty acid content, especially in whole milk, during storage (3 days for raw milk and 21 days for pasteurized milk), foaming properties and foam structure were almost unchanged in all types of milk.

Addition of foaming agents

Foaming agents are referred to any substances, except for the ones which have already been discussed in previous sections, which are intentionally added to milk to alter the properties of milk (e.g. viscosity, pH and mineral balance) and interfacial adsorbed layers, subsequently altering the foamability and/or foam stability. However, the addition of agents, especially at high concentrations, can destroy the desirable characteristics of the product, thus the type and concentration of the agent should be optimized depending on a particular application.

Polysaccharides

As mentioned above, the rate of drainage of liquid film in foam could be minimized through an increase in liquid viscosity (Huppertz 2010; Walstra 1989). Therefore, an addition of high water adsorption substances such as hydrocolloids or polysaccharides can improve foam stability. It was reported that addition of xanthan gum (0.05–0.20%, w/w) significantly increased viscosity of milk, resulting in a noticeable increase in foamability, without affecting the sensory properties of the product, but markedly decreased foamability due to reduced diffusion rate of surfactants at high viscosity (Khezri, Shahriari, and Shahsavani 2017). Similar results were also reported for lactose (> 20%, w/w), κ -carrageenan (0.01–0.03%, w/w), κ -carrageenan (0.5%, w/v), and xanthan gum (0.05–0.2%, w/w) as they were added to WPI (Zhu and Damodaran 1994c), reconstituted SMP (Kamath 2007) and β -lactoglobulin (Carp et al. 2004), and WPI (Mott, Hettiarachchy, and Qi 1999), respectively. The added polymers not only induce the viscosity increase, but also interact with themselves or with existing proteins to enhance foaming properties. Proteins can form reversible and permanent complexes with polysaccharides *via* attractive electrostatic interactions and covalent bonding, respectively. The reversible protein-polysaccharide complexes are formed from a mixture of proteins and polysaccharides with the same or different charges while the permanent complexes are produced as a result of chemical reactions between lysine groups of proteins with ester groups or reducing sugars of polysaccharides (Dickinson and Izgi 1996).

Depending on the protein properties, that govern the properties of the protein-polysaccharide complexes, foaming properties of protein-polysaccharide complexes vary widely. It was reported that covalent complexes of dextran with bovine serum albumin (BSA), lysozyme and β -casein under same conditions exhibited different foaming behaviors. Unlike lysozyme-dextran complexes which had substantial improvement in foamability and foam stability, β -casein-dextran complexes had a negative effect, while BSA-dextran complexes had a marginal enhancement in foaming properties (Dickinson and Izgi 1996). For electrostatic complexes of proteins and polysaccharides, it was found that adding anionic non-surface active polysaccharides, such as sodium alginate and λ -carrageenan, into WPI and WPC at concentrations up to 0.1% (w/w) markedly improved their foamability and foam stability in which λ -carrageenan showed a significantly higher enhancement. Although both sodium alginate and λ -carrageenan have ability to increase the viscosity of the aqueous solution, which is a barrier to drainage of liquid film, only λ -carrageenan can form hybrid soluble complexes with proteins in the aqueous phase and at the air-water interface, which reduces the disproportionation or collapse of air bubbles (Perez et al. 2010). An improvement in foamability and foam stability of sodium caseinate at pH 5.0 as mixed with glycomacropeptide polymer was also reported (Morales, Martinez, and Pilosof 2017). The synergistic interactions of a mixture of casein glycomacropeptide polymer and sodium caseinate in the aqueous phase reduced the aggregation state of sodium caseinate so that the size of

Table 4. A summary on reported studies on effects of minerals on foamability and foam stability of milk and milk proteins.

Samples	Minerals and concentrations	Foamability	Foam stability	References
RSMP, 10% (w/v)	EDTA <ul style="list-style-type: none"> 0-10 mM 10-60 mM 	<ul style="list-style-type: none"> Marked improvement No further improvement 	<ul style="list-style-type: none"> Marked improvement No further improvement 	Ward et al. (1997).
RSMP, 9.6% (w/w)	<ul style="list-style-type: none"> Na₂HPO₄, 0.21 mol/kg Citrate, 0.21 mol/kg CaCl₂, 0.21 mol/kg 	<ul style="list-style-type: none"> Marked improvement Marked improvement Declined 	<ul style="list-style-type: none"> Marked improvement Marked improvement Declined 	Augustin and Clarke (2008)
RSMP, 8.5% (w/w)	EDTA, sodium hexametaphosphate and citrate, 10-20 mM	No effect	<ul style="list-style-type: none"> No effect at foaming temperatures from 5-25°C. Marked improvement at foaming temperatures from 45-85°C 	Kamath (2007)
<ul style="list-style-type: none"> α-lactalbumin, 0.001% (w/w) β-lactoglobulin, 0.001% (w/w) α-lactalbumin, 15% (w/w) β-lactoglobulin, 15% (w/w) 	<ul style="list-style-type: none"> CaCl₂, 10-20 mM EDTA, 5.0 mM CaCl₂, 5.0 mM 	<ul style="list-style-type: none"> Significantly decreased Significantly decreased 	Improved Improved	Ibanoglu and Ibanoglu (1999)
<ul style="list-style-type: none"> α-lactalbumin, 15% (w/w) β-lactoglobulin, 15% (w/w) 	CaCl ₂ , 0.4 mM	Significantly decreased	Improved	Luck et al. (2002)
WPI, 5% (w/v)	NaCl, 0.02-0.15 M	Markedly decline	Markedly decline	Zhu and Damodaran (1994c)
WPI, 0.55% (w/w)	NaCl <ul style="list-style-type: none"> 0.0-0.1 M 0.1-0.8 M 	<ul style="list-style-type: none"> Improved Declined 	Not determined	Zhang et al. (2004)
RSMP, 1.4% (w/w)	NaCl, 0-0.8 M	Improved	No effect <ul style="list-style-type: none"> Markedly improved as compared to no CaCl₂ Highest stability 0.02-0.04 M Declined stability > 0.04 M Markedly improved as compared to no MgCl₂ 0.02-0.06 M: Increased 0.06 M: Highest > 0.06 M: Declined 	Marinova et al. (2009)
WPC, 0.1% (w/w)	NaCl, 0.15-0.4 M	No effect		Zhu and Damodaran (1994a)
WPI, 5% (w/v)	CaCl ₂ , 0.02-0.20 M	Improved		
	MgCl ₂ , 0.02-0.10 M	Improved		
WPI-Xanthan (5%,– 0.05%, w/w)	NaCl, 0.05-1.0 M	Improved	Improved	Mott et al. (1999)

Where, RSMP = reconstituted skim milk powder

WPI = Whey protein isolate

WPC = Whey protein concentrate

sodium caseinate particles was reduced by more than ten-fold. The small aggregates were more efficient in incorporation of liquid into foam and stabilization of the interfacial films. In addition, similar synergistic interactions of biopolymers on foamability and/or foam stability were observed for a mixture of casein glycomacropeptide and β -lactoglobulin (Martínez et al. 2012), a mixture of xanthan gum and WPC (Martínez-Padilla et al. 2015) and a mixture of WPC and pectin (Mishra, Mann, and Joshi 2001; Oduse et al. 2017).

Mineral balance

Mineral salts have a significant impact on the conformation of proteins (caseins and whey proteins), their stability, and their state of association and distribution between the colloidal and serum phases of milk through specific and non-specific interactions (Augustin 2000). Structure and stability of the milk proteins have predominant roles in governing the functional properties of the milk, and the foaming properties are highly determined by the types of proteins and their availability on interfacial regions. Thus, addition or removal of milk salts provides a means of manipulating foaming properties of milk (Zayas 1997). Studies on effects

of mineral addition on foaming properties of milk and protein solutions are summarized in Table 4.

The addition of calcium-chelating agents leads to removal of colloidal calcium phosphate from the casein micelles and a release of micellar caseins into the serum phase of milk. It was reported that an addition of trisodium citrate and ethylenediaminetetraacetic acid (EDTA) at concentration of 10 mmol/kg released about 20 and 30% caseins from the micelles, respectively (Udabage, McKinnon, and Augustin 2000). However, EDTA released not only caseins from the micelle, but also denatured whey proteins, which are often found in high temperature treated milk. The dissociation of caseins into the serum and/or denaturation of whey proteins results in an increase in the amount of the proteins available for the formation and stabilization of the foam. Thus, whipping properties in terms of foam overrun and stability of reconstituted SMP (10%, w/w) were markedly enhanced with an increase in EDTA concentration up to 10 mmol/L (mM), a further increase in the EDTA concentration did not improve foamability and foam stability (Ward et al. 1997). Similar results were also reported for an addition of citrate (citric acid, trisodium and tripotassium salts) and disodium hydrogen phosphate at concentrations of 0.1-0.5 mol/kg

serum solids by which the steam-frothing and whipping properties of reconstituted SMP (9.6%, w/w) were significantly enhanced. Interestingly, similar effects on foaming properties could be achieved through the addition of citrates into skim milk concentrates prior to spray drying to produce the powder (Augustin and Clarke 2008). However, Kamath (2007) reported that at foaming temperatures between 5–25 °C, an addition of calcium-chelating agents (e.g. EDTA disodium salt, sodium hexametaphosphate and trisodium citrate dihydrate) at concentrations of 10–20 mmol/L had no effect on foamability and foam stability. Nevertheless, at higher foaming temperatures between 45–85 °C, although calcium-chelating agents did not affect foamability, but markedly declined foam stability. Preferential loss of β -caseins (which are more surface active than intact casein micelles) from the micelles caused by calcium-chelating agents led to increased adsorption of highly surface active β -caseins on the interface by which it prevents aggregation of casein micelles (which is an important determinant of foam stability).

An addition of 0.21 mol CaCl_2 /kg serum solids into reconstituted SMP (10%, w/w) completely depressed the formation and stability of foam (Augustin and Clarke 2008). However, in another study Kamath (2007) reported that an addition of 10–20 mmol/L CaCl_2 significantly decreased foamability, but improved foam stability of reconstituted SMP (8.5%, w/w). Nevertheless, heating of milk containing such concentrations of CaCl_2 up to temperatures higher than 65 °C causes the coagulation of milk. This suggests that CaCl_2 at high concentration is unsuitable to be used as a foaming agent for high temperature applications. For individual whey proteins, such as α -lactalbumin and β -lactoglobulin, it was reported that addition of EDTA (5.0 mM) and CaCl_2 (5.0 mM) (Ibanoglu and Ibanoglu 1999), and CaCl_2 (0.4 M) (Luck, Bray, and Foegeding 2002) dramatically improved foamability and foam stability. Similar findings about enhancement of foaming properties of WPI (5.0%, w/w) added with CaCl_2 (0.02–0.2 M) and MgCl_2 (0.01–0.1 M) were reported (Zhu and Damodaran 1994a). Changes in protein conformation induced by interactions with Ca^{2+} and Mg^{2+} ions and polymerization *via* ionic bridges are reasons for enhancement of the foaming properties of WPI. Due to a greater binding affinity of proteins to Ca^{2+} ion than Mg^{2+} ion, foam stability induced by Ca^{2+} ion was much higher than that brought by Mg^{2+} ion. Surprisingly, it was found that the highest enhancement effect of CaCl_2 and MgCl_2 on foaming properties was only obtained as foam was produced immediately after salts were added (Zhu and Damodaran 1994a). Delaying the foam process after salt addition progressively decreased the enhancement effects of salts.

Another salt affecting foaming properties of milk is NaCl. The foamability and foam stability of WPI were progressively decreased with an increase in the concentration of added NaCl in a range of 0.02–0.15 mol/L. This is probably caused by the dissolution of whey proteins, especially β -lactoglobulin, in the salt solution which reduces the amount of whey proteins available at interfacial regions

(Zhu and Damodaran 1994c). However, Zhang, Dalgleish, and Goff (2004) reported that an addition of NaCl up to 0.1 mol/L markedly increased foamability of WPI, and a decrease in the foaming ability of WPI occurred only at concentrations higher than 0.1 mol/L. But, at the same NaCl concentrations (0.1–0.8 mol/L), foamability of reconstituted SMP showed a continuous improvement. In addition, it was reported that an addition of 0.15–0.4 mol/L NaCl did not show any substantial effect on foaming behavior of WPC, but greatly enhanced foam capacity and stability of sodium caseinate (Marinova et al. 2009). The findings of these studies illustrate that the effects of NaCl on foaming behavior are dependent not only on concentration of salt but also types of proteins present in the foaming system.

Proteolysis

Proteolysis is a breakdown of proteins into peptides and amino acids by proteolytic enzymes known as proteases (Varshavsky 2001). In terms of foaming, the formed peptides with low molecular weight diffuse to the interfacial regions to create foam faster than proteins, but compete and/or interfere with proteins in the formation of highly viscoelastic film to stabilize the foam. Thus, proteolysis of milk can improve foamability but reduce foam stability (van der Ven et al. 2002). Depending on the degree of protein hydrolysis (DH), which in turn was determined by hydrolysis conditions, many peptides with different properties and functionalities are produced. For example, hydrolysis of β -casein by plasmin (3% w/v β -casein, enzyme/substrate \approx 1/2300 w/w, pH 6.8, 40 °C) produced a mixture of strongly hydrophobic, amphipathic and strongly hydrophilic fractions. Synergistic effects of these fractions significantly improved the foamability and foam stability of the hydrolyzed β -casein (Caessens et al. 1997). As a result of proteolysis, foaming properties of hydrolysates are typically governed by DH (Kilara and Panyam 2003). It was reported that a low degree (< 2.6% DH) hydrolysis of sodium caseinate by alcalase® enzyme did not affect its foaming properties while both foamability and foam stability declined sharply at higher DH (Ewert et al. 2016). However, an increase in foam expansion and a decline in foam drainage was reported for sodium caseinate hydrolyzed by protease obtained from *Bacillus subtilis* at 0.5–1.0% DH. Hydrolysis at higher than 1% DH resulted in poor foaming properties (Slattery and Fitzgerald 1998). For whey proteins proteolysed by papain, foam stability was a function of DH in which it markedly increased with increasing DH up to 3.0%, and then dramatically dropped as DH was beyond this value. Liberation of β -lactoglobulin, α -lactalbumin and especially low molecular weight peptidic fragments from whey proteins during proteolysis was possibly the reason for the changes in foam stability (Lieske and Konrad 1996). Not only DH, type of enzyme used for hydrolysis also affects the foaming behavior of the hydrolysates because the proteolytic enzyme determines molecular weight, hydrophobic or hydrophilic characteristics, and composition of peptides. It was found that WPI hydrolyzed by alcalase®, chymotrypsin, trypsin,

pepsin or acid fungal protease at 2.5–3.0% DH showed significantly improved foaming capacity, but the enhancement of foam stability was only observed for those hydrolyzed with alcalase®, chymotrypsin and trypsin (Althouse, Dinakar, and Kilara 1995). By studying effects of 11 types of proteolytic enzymes on DH and foaming properties of casein and whey protein hydrolysates, van der Ven et al. (2002) found that the hydrolysates with higher proportion of amphiphilic peptides and higher molecular weight peptides exhibited a high foamability and high foam stability, respectively. Moreover, effect of proteolysis on foaming behavior is also dependant on pH. It was reported that at pH 5.0 and 7.0, native β -lactoglobulin did not exhibit any difference in foamability and foam stability. However, hydrolysis of β -lactoglobulin to a DH of \sim 4.0% markedly affected its foam stability. As compared to native β -lactoglobulin, foam stability of the hydrolyzed β -lactoglobulin declined by about 50% at pH 7.0, but increased by 30% at pH 5.0 (Corzo-Martínez et al. 2017). Similar results were also reported for whey proteins, in which regardless of the DH values (1.0–5.0%), hydrolyzed whey proteins at pH 4.0 produced much more stable foam than that at pH 2.0 and 6.0 (Lieske and Konrad 1996). From these studies, it can be inferred that at pH close to pI, impact of pH on foam stability is more profound than that of DH. Minimization of repulsive electrostatic interactions between molecules at pH near to pI promotes intermolecular hydrophobic interactions on the interface, resulting in high foam stability.

It is worth noting that proteolysis of milk can be caused by native enzymes (such as plasmin and those derived from somatic cells) or bacterial enzymes (Chramostova et al. 2017). Peptides arising from proteolysis of proteins by plasmin, together with a mixture of heterogeneous proteins (glycoprotein and hydrophobic constituents) constitute to proteose-peptone fraction (Innocente, Biasutti, and Blecker 2011). Considering foaming, proteose-peptone fraction is detrimental to the foaming properties of milk. An addition of 0.01–0.2% (w/w) proteose-peptone was found to significantly reduce foam stability of WPI, but did not affect its foamability (Zhu and Damodaran 1994c). Negative effects of proteose-peptone on foaming property of raw milk were also reported (Buccioni, Minieri, and Rapaccini 2013). In milk, proteose-peptone content varies in relation to somatic cell counts. High somatic cell counts were found in milk characterized by a lower foaming properties and a high amount of proteose-peptone (Buccioni, Minieri, and Rapaccini 2013; Summer et al. 2003). However, almost no study on foaming behavior of milk with different somatic cell counts can be found in the literature. Similarly, although it is well documented that psychrotrophic bacteria contaminating milk after milking have the ability to form hydrolytic thermostable enzymes that break down the major constituents of milk (Samaržija, Zamberlin, and Pogačić 2012), by which foaming properties of milk could be affected, it is hard to find any study in the literature about relationship of microbial quality and foaming ability of milk.

Conclusion

From this review, it can be seen that foaming of liquid milk is extremely complicated as it is determined by multiple factors, particularly protein content, ratio of caseins to whey proteins, casein micelle size, pH, the presence of other compounds competing with milk proteins such as low molecular weight compounds and polysaccharides, fat globule size (normal homogenization), foaming methods, heat treatment before and during foaming, aging of milk, proteolysis and so on. These factors, alone or in combination, vary in their impact on the conformation, structure and intermolecular interaction ability of milk proteins which play an integral role in formation and stabilization of the foam. Therefore, among foaming driving factors, some affect the foamability while others determine the foam stability. An understating of these factors in totality could help to control the foaming process of liquid milk on demand for a particular application.

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