Research Progress of Air-water Interface Stability in Food Foam System

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Abstract: The foam dispersion system is widely used in many kinds of food processing fields and give good texture and sense for food. This paper summarized this formation mechanism, the effect mechanism of internal factors (surface tension, surface viscoelasticity) and external factors (temperature, pH, surfactant, ionstability) on stability of foam system, and the progress of effect of polysaccharide hydrocolloids co-regulating protein on stability of foam system. The aims was to provide theory support for developing natural surfactant and obtain expected foam texture in food system. In order to promote the application of polysaccharides hydrocolloid surfactant in the field of foam food processing.

1 INTRODUCTION

In daily life, the macro behavior of many foods, such as their stability, rheological properties and structure, is related to the state of structural units. As one of the most common structural units in multiphase food system, the foam system plays a vital role in beer, inflatable candy, ice cream, baking products and other foods. The foam system not only gives the superiority of food organization structure and appearance, but also benefits chewing and food flavor transmission. At the same time, the addition of air can also reduce energy intake to a certain extent and meet modern people's pursuit of healthy diet (Liu 2009). Because foam is a typical thermodynamic instability system of air-liquid two phase, the high specific surface area and surface free energy of air-liquid interface lead to unstable foam (Li 2020). Therefore, how to obtain stable (metastable) foam system in actual food production and processing is a problem that needs to be further studied.

2 FORMATION AND INSTABILITY OF FOAM SYSTEM IN FOOD

2.1 Formation of Foam System

The foam in food is a dispersive system composed of bubbles separated by liquid membrane, where liquid or semisolid is a continuous phase and gas is dispersed phase (Diao *et al*. 2021). The foam structure is shown in Figure 1. Foam formation requires four conditions: gas, water, surfactant and energy. Full contact between gas phase and water phase is a necessary condition for foaming. Energy increase the interfacial area between the two phases. The function of surfactant is to adsorb on the air-liquid interface to form an elastic liquid film with a certain thickness, reduce the surface tension and maintain the stability of the air-liquid interface.

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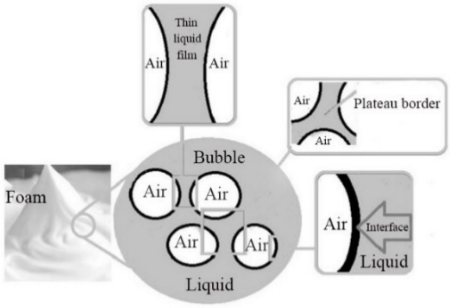


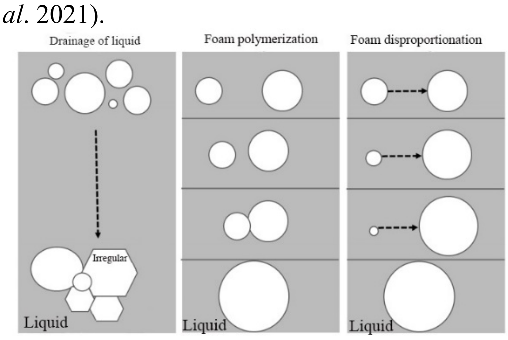
Figure 1: Scheme of the foam structures (Li 2020).

2.2 Instability of Foam System

Because of the high surface free energy of the foam system in the air-water boundary, the foam surface is unstable. According to the principle of Gibbs free energy, in order to reduce the interfacial area, the surface free energy will decrease spontaneously, resulting in the loss of water film, polymerization and disproportionation of the bubble film, which will cause the instability of the foam system (Murray & Ettelaie 2004). As shown in Figure 2:

- Drainage of water is the process of separation of air-water two phase in foam system due to different density (Conroy *et al*. 2013). Loss of fluid can result in gradual drying of foam;
- Polymerization is the phenomenon that the film between two adjacent bubbles breaks, resulting in the merger of two bubbles (Murray *et al*. 2006).
- Disproportionation is the transfer of air in small bubbles to large bubbles, resulting in the disappearance of small bubbles (Langevin *et al*. 2017).

These three phenomena exist simultaneously in the foam system and contain each other. But no matter which mechanism is dominant, the final equilibrium state of the foam system will be separated into an independent water phase and air phase (Diao *et al*. 2021).



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3 FACTORS AFFECTING THE STABILITY OF FOOD FOAM SYSTEM

Evenly distributed foam often makes food texture fine, lubricated, with a certain brightness, but also enhances the flavor components divergent and observable (Li *et al*. 2020). It constitutes the main sensory attraction of consumers. Stable beer foam can not only give consumers the sense of enjoyment, but also reduce the overflow of beer flavor substances. It prevents the direct contact of oxygen and beer in the air and oxidize, so as to ensure the quality of beer (Han 2017). Good foaming and foam stability help to form the texture of ice cream and extend the storage period of ice cream (Lian *et al*. 2020). In inflatable chocolate, small and stable foam will make the chocolate more lubricate and delicate, and it will also be very different in color (Liu2009). Therefore, the stability of the foam system is critical to the quality of food. However, foam stability is easily affected by internal and external factors such as surface tension, surface viscoelasticity, temperature, pH and surfactant.

3.1 Formation of Foam System

3.1.1 Surface Tension

With the formation of foam, the surface area of liquid increases and the surface potential energy increases (Zhan *et al*. 2020). The lower surface tension is favorable for improving the foam stability. The Laplasse equation shows that the smaller the surface tension and the smaller the pressure difference, the more stable the foam is. Xiao Xia (Xiao 2013) randomly selected 7 kinds of wine samples from the market to determine the foam retention and surface tension. The results showed that the surface tension of the wine with good foam stability was poor. At the same time, as the storage period lengthened, the foam retention gradually decreased, and the surface tension gradually increased.

3.1.2 Surface Viscoelasticity

Surface viscosity refers to the viscosity of the molecular layer of foaming agent on the liquid membrane, which is produced by the interaction between hydrophilic groups and water (Li 2014). The greater the adsorption force of surfactant molecules on the air-liquid interface, the higher the surface viscosity and the better the elasticity of the membrane. The surface viscosity directly determines the drainage rate of the liquid film, thereby affecting the stability of the foam to a certain extent. The greater the surface viscosity, the smaller the drainage velocity, and the more stable the foam is (Cilurzo *et al*. 2019). However, for the production and processing of ice cream, if the viscosity of the system is too high, the ice cream material will be too viscous. During the freezing process, it is difficult for a large number of air to be evenly distributed in ice cream, resulting in low expansion rate and poor taste of the product (Zhan *et al*. 2020).

Surface elasticity refers to the ratio of the stress on the surface to its strain. It means the tendency or ability of the surface to return to the initial state after deformation under external force (Wu 2017). Therefore, the surface elasticity of the foam liquid film can also be considered as 'self repairing' ability to resist external interference. When the liquid film of the foam is disturbed, this 'self repair' capability is embodied in two aspects:

- With the increase of the area of the foam liquid film and the decrease of the surface density of the surfactant, the local surface tension increases, and the surface tension gradient formed has the tendency to shrink the liquid film, which is called the Gibbs effect;
- Under the action of surface tension gradient, surfactant molecules migrate from regions with higher density to regions with lower density, which is called Marangoni effect (Wang & Guo 2007).

Generally speaking, Gibbs elasticity is more suitable for measuring the stability of static foam, while Marangoni elasticity is often used to measure the stability of dynamic foam. Zhang (Zhang 2012) found that the interaction between Tween 20 and BSA and the formation of gel like interface network structure enhanced the surface elasticity of the adsorption film, increased the ability to resist external interference, reduced the liquid film drainage rate, and further improved the stability of the foam. Because there is no adsorbed surfactant on the surface, the pure aqueous film cannot adjust the surface tension gradient through the movement of surfactant or the contraction of the film when disturbed by the outside world, so it does not have the ability of 'self repair' (Li 2014).

3.2 Influence of External Factors

3.2.1 Temperature

The change of temperature significantly affects the properties of liquid film. Most of the foam is unstable at high temperature. As the temperature increases, the surface viscosity of the liquid film decreases, and the discharge rate increases, resulting in the decrease of foam stability (Li 2014). Han (Han 2017) explored the effect of different pretreatment temperatures on the stability of beer foam. It was found that the stability of beer foam decreased with the increase of temperature, and the higher the temperature, the worse the foam stability. The reason may be that the solubility of CO_2 in beer decreases after the temperature rises, and the dissolution of CO_2 after ultrasonic oscillation is faster, resulting in larger volume of individual bubbles formed by beer foaming, and the decrease of surface viscosity and foam stability of beer foam.

3.2.2 pH

The change of pH affects the ionization of the foam system. Ionization is closely related to the interaction in the whole solution, the adsorption of molecules at the air-water interface and the interaction at the interface. Li et al. (Li, *et al*. 2017) found that the egg white protein produced excessive negative charges in alkaline solution, which increased the static repulsion between protein molecules and weakened the stability of the foam system. However, for egg yolk protein, the increase of pH is helpful to the dissociation of insoluble yolk protein particle aggregates, improve its adsorption capacity at the air-water interface, reduce the surface tension, and help to enhance the stability of the foam system. The results are quite different from those of the egg white foam system in alkaline solution. Kuropatwa et al. (Kuropatwa *et al*. 2009) found that whey protein and egg white protein complex at pH 9.0 had higher foaming and foam stability. This is because the electrostatic interaction of proteins has occurred before foaming, and the protein of the composite system is adsorbed at the air-water interface. Under alkaline conditions, expanded β-Lactoglobulin monomer can increase the interaction of egg white protein whey protein complex. Compared with neutral conditions, the foaming property and foam stability of the composite system increased. However, Li et al. (Li 2009) tested the foam stability of benzyl phosphate under different pH. Compared with the results of pH=5.5 and pH=7.2, it was found that the stability of pH=5.5 foam was good.

3.2.3 Surface Active Agent

In order to make foam easily generated and stable, it is necessary to add stabilizer to the system, usually surfactants. Its existence not only makes foaming easy, but also makes foaming speed faster than bubble breaking speed, thus obtaining stable foam (Li 2020). As shown in Fig. 3, the foam generated by pure water will burst quickly after reaching the interface. However, the foam formed by surfactant solution can be stabilized. This is because a large number of surfactants can adsorb to the air water interface, reduce the surface tension, and form a viscoelastic interfacial film around the bubble through non covalent molecular interactions and covalent two sulphide crosslinking, thus forming and stabilizing the foam (Perez *et al*. 2006). Gao (Gao 2020) compared the pure rice flour bread with the rice flour bread added with pullulan polysaccharide, and found that the addition of pullulan polysaccharide improves the characteristics of rice flour bread, such as high hardness, poor elasticity and difficult to chew. The reason may be that pullulan as a surfactant, combined with water, form a more compact viscoelastic colloid in the continuous phase, increase foam stability, and better preserve the gas generated during fermentation. Schmidt et al. (Schmidt *et al.* 2010) studies found that the interfacial activity of the compound formed by rapeseed protein and pectin was higher than that of pure rapeseed protein, and the thicker interfacial film could be formed at the air water interface, resulting in the decrease of water permeability and the rise of the stability of the foam.

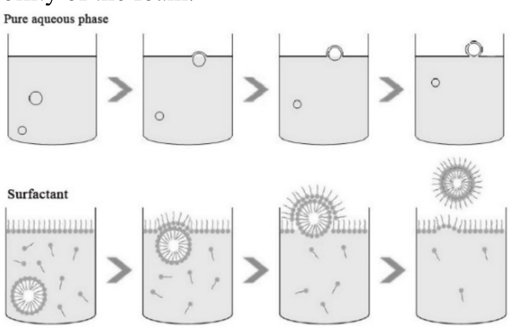

Figure 3: Rise of bubbles in pure aqueous phase and surfactant solution (Cilurzo et al. 2019).

3.2.4 Ion

The effect of inorganic salts on foam stability is mainly through interaction with surfactant (Yu *et al.* 2010). The addition of inorganic salts will introduce ions which with charge opposite to surfactant headgroup. When the amount of inorganic salt is small, the charged ions will be adsorbed on the surface of the surfactant base, reducing the electrostatic repulsion between the adjacent surfactants, making them close to each other, thus reducing the interfacial tension. This will help to enhance the stability of the foam (Teng *et al*. 2005). However, when the content of inorganic salt is too high, the combination of excess inorganic salt ions and surfactants may lead to the failure of surfactant or destroy the electric double layer structure, which is not conducive to the stability of foam (Liu 2011). Wu Gang (Wu 2017) studied the mechanism of the effect of inorganic salts on the foam stability of surfactant and its composite system. It was found that the addition of sodium salt had a negative effect on the stability of surfactant foam, and the higher the concentration of sodium salt, the more unfavorable to foam stability. Low concentration of calcium salts and magnesium salts had a favorable effect on foam stability, and magnesium salt had greater impact than calcium salts. When high concentration, the stability of surfactant foam would also be adversely affected. The higher the concentration, the worse the foam stability.

4 POLYSACCHARIDE HYDROCOLLOID REGULATES THE STABILITY OF FOAM SYSTEM

Because of its excellent foaming properties, solubility, emulsification and gelation, the protein has been widely used as a surfactant in the production and processing of foam food (Narsimhan & Nin 2018). However, individual protein molecules are not ideal candidates for stable foaming systems because they cannot fully adjust the high Laplace pressure difference at the air-water interface (Shankaran & Chinnaswamy 2019). Since most high molecular weight polysaccharides are hydrophilic, they do not have much adsorption tendency at the air-water interface. However, they greatly enhance the stability of the dispersion system through their thickening or gelling properties. Therefore, in the food industry, polysaccharides are used to synergistic protein maintain the stability of the foam system and emulsion system (Dickinson 2003). A classic example is the use of pectin to stabilize casein micelles in yogurt. Due to electrostatic interaction, negatively charged pectin molecules are adsorbed on casein micelles and prevent casein from acid-induced aggregation due to electrostatic and spatial repulsion (see Fig. 4) (Renate *et al*. 2005). Among them, polysaccharides act as two roles. One is to control the rheological properties of the continuous phase. The other is to increase the thickness of the adsorption film, which reduces the rate of thinning of the bubble film and increases the stability of the foam (Sadahira, *et al*. 2018). The addition of polysaccharide water colloid significantly improves the viscosity of gluten free dough and hinders the escape of gas during fermentation, so as to improve the quality of bread and prolong the shelf life of bread, which solves the dietary problems faced by celiac patients to a certain extent (Niño-Medina *et al*. 2019).

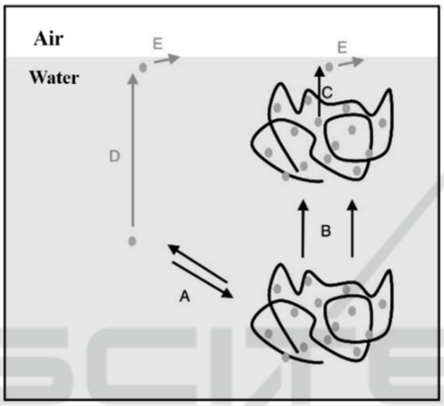

Figure 4: Model for polysaccharide controlled protein adsorption at the air/water interface (Renate *et al*. 2005) (A：partition free protein and protein bound to polysaccharide, B：diffusion of protein/polysaccharide complexes in bulk, C：availability of complexed protein for interface, D：diffusion of free protein in bulk, E：kinetic barrier for protein adsorption)

From the existing research, the application of polysaccharide hydrocolloid in the stabilization of food foam system is based not only on its electrostatic interaction with protein, but also by the covalent grafting products formed by Maillard reaction with proteins, which play an important role in modifying the functional properties of proteins (Diao *et al*. 2021). The amino group on the protein and the carboxyl group of reducing sugar bind to each other can significantly improve the solubility and oxidation resistance of protein, and further improve the stability of foam system (Yu 2016). In the process ，the amino group on the protein and the carboxyl group of reducing sugar bind to each other can significantly improve the solubility and oxidation resistance of protein, and further improve the stability of foam system (Yu 2016). At present, many studies have reported that proteins are modified by various food grade substrates to obtain a stable foaming system. Ovalbumin pullulan cement shows better foaming performance and surface activity than natural protein (Sheng *et al*. 2020). A large number of studies have shown that the increase of protein foaming ability by glycosylation reaction is mainly due to the covalent connection between sugars and proteins, which increases the hydrophilic groups in proteins, which may lead to the increase of protein solubility, or the formation of protein melting spherical structure caused by mild heat treatment, which improves the hydrophobicity of protein surface (An *et al*. 2014, Murray 2007).

Because proteins usually have high surface activity, most protein microgel particles also have surface activity, and their Pickering particles can adsorb efficiently at the air-water interface and require very high desorption energy. Therefore, it has higher viscoelasticity compared with the interfacial film formed by single protein adsorption. Microgel particles can also be composed of polysaccharides with gel characteristics. Although most polysaccharides are non surface active substances, they can be combined with other components, such as proteins or lipids, so as to achieve good adsorption effect (Li 2020). From the perspective of food, protein and polysaccharides have great advantages as microgel particles, which can control the size of surface active particles reasonably by controlling the size of complex biopolymers or their mixtures (Chen *et al*. 2017). In the presence of protein / polysaccharide complexes, the foam stability increases due to the formation of viscoelastic colloids in continuous phases (Zhan *et al*. 2019). The protein / polyphenol complex which whey protein with gallic acid (GA) and epigallocatechin gallate (EGCG) have a similar strengthening effect (Cao & Xiong 2017).

Despite the above findings, the foam formation properties of the composites are not always consistent with their foam stability. For example, tannic acid improves foam stability, but it inhibited the foam formation of sodium caseinate (Zhan *et al*. 2018). Therefore, high performance food hydrocolloids exhibiting excellent foaming and foam stability are still being constantly excavated.

5 CONCLUSIONS

In the food industry, the stability of the foam system will directly affect the quality of the interface leading foods. Therefore, controlling the stability of foam system, regulating protein aggregation behavior and understanding the relevance between surfactant and foam system play an important role in guiding the development of foam food industry. Future research on food foam system can focus on establishing a relationship model of protein (polysaccharide) molecular polymer foam system, and clarify the mechanism between the three. It aims at precisely regulating protein nano polymer in order to obtain an ideal foam system, and provide a theoretical basis for the application of foam food in the food industry.

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