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Oleofoams: Mechanism, Characterization, Application and Recent Research Trends

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ABSTRACT

Edible oleofoams system gaining more interest as an alternative for conventional solid fat foods due to its low-fat content, healthier functional properties, improved rheological properties, new sensory properties and long-term stability. In this review we discuss the formation principle, structurization protocols, applications, stabilization mechanisms and characterization using advanced techniques. The works on edible oleofoams still need to be explored because of its very scarce research findings when compared to aqueous foams regardless of its promising application as potential food ingredient in future food processing sector. These advances reduce the usage of hardstock fats, which are linked to harmful health effects and negative customer impression. New fundamental insights through research support providing possibilities in designing novel food products based on oleofoams to expand its potentiality in the area of food processing.

Keywords: Oleofoams; Structurization; Stabilization; Characterization; Future Food

Introduction

The thrusts for excitement in the pursuit of reducing, alternating, eliminating, and biomimicry of trans fatty acids and saturated fatty acids from the food system of human consumption have gained impetus in ongoing research investigations on the structuring of edible oils. Effective eradication of trans fatty acids from the human diet has become a major concern due to its adverse effects on health and lifestyle disorders such as obesity, cardiovascular disease, metabolic syndrome, and type 2 diabetes mellitus. Countries such as the United States and Canada took it seriously, making the addition of trans fatty acids to food illegal and removing partially hydrogenated oil from the generally recognized as safe list (Dickinson, et al. [1]). At this moment in time, it has become highly intricate in eliminating or reducing saturated fatty acids in the food industry. Saturated and trans fatty acids account for much of the functionality and properties of solid fat in food processing industries. Food manufacturers are scrambling to find alternative ways to reduce or eliminate solid fats as an ingredient in their products while maintaining organoleptic properties and satisfying consumer demand. The presence of fatty acids in triacylglycerols form results in the assembly of particles with a diameter of more than 1 µm. A supra-colloid particle network called "fat crystal network" is the outcome of the solid structuring of fat, which prevents exudation of liquid fat entrained in the network (Scharfe, et al. [2]). The key research trends and out-coming solution is the alternative structuring of edible oil as "alternative networking" for the fat crystal network.

The key research trend and out-coming solution is the alternative structuring of edible oils into complex colloidal systems of liquid foams based on the dispersion of gaseous bubbles in a continuous liquid phase entraining surface active materials (Fameau, et al.

[3]). This advancement of edible oil liquid foams, called oleofoams, involves incorporation of air bubbles in a continuous oil phase (oleogels) containing mono or diglycerides, triglycerides, fatty acids, long chain fatty alcohols, monoacylglycerols, diacylglycerol fatty ester, sucrose ester, natural waxes, proteins, and polysaccharides (Fameau, et al. [4]). Oleofoams will become a major breakthrough in creating food products by reducing solid fat usage, thereby providing new texture and organoleptic properties. It works by reducing and replacing the saturated and trans fatty acid content of food systems in the view of enriching the nutritional aspects. The significance of oleofoams is not only restricted to textural change and reduction of fat content; it also has a novel long-standing stability even above the room temperature, which could be achieved by limited or nil usage of additives. Oleofoams tend to be less susceptible to microbial spoilage because of their composition, which contains oil without water (Murray, Brent [5]). Edible oil structure is still in its infancy as a study subject, but it has already piqued the interest of academicians and industrial specialists. Oil structuring aims to substitute solid fats in food items with materials that can trap and structure liquid oil to approximate the functions of fat. Although this technique has good prospects, it has a critical drawback in finding food-grade ingredients that can be employed in edible products. This review will discuss the recent studies, current state of knowledge, and future scope of edible oleogels and oleofoams used in food processing. The benefits of oleogel and oleofoam based system has been presented in Figure 1.

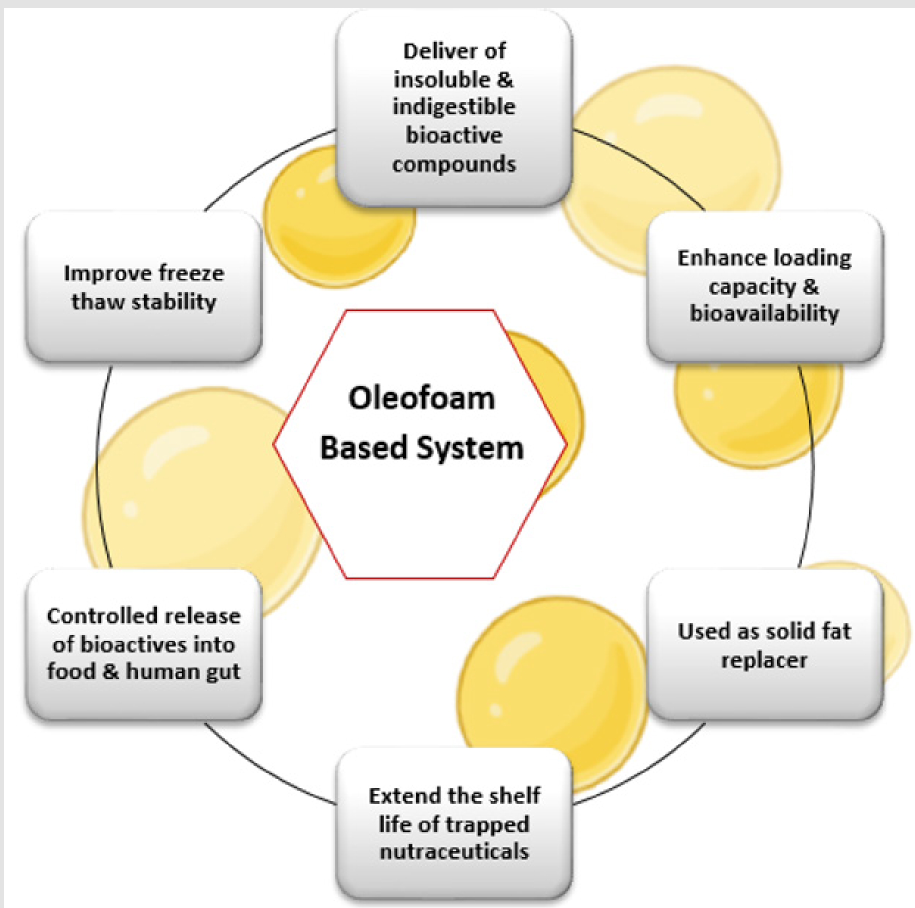

Figure 1: Schematic representation on benefits of oleogel & oleofoams based system.

Oleofoams

Oleofoams, edible air-in-oil system, non-aqueous foams, are gaining interest as promising novel healthier ingredient which acts as low-calorie fat replacers in formulation of food products. Reduction in the level of saturated and trans fatty acids through oleofoams reduces health concerns and various lifestyle disorders. Structuring and developing of oleofoams involves two step procedures (Figure 2),

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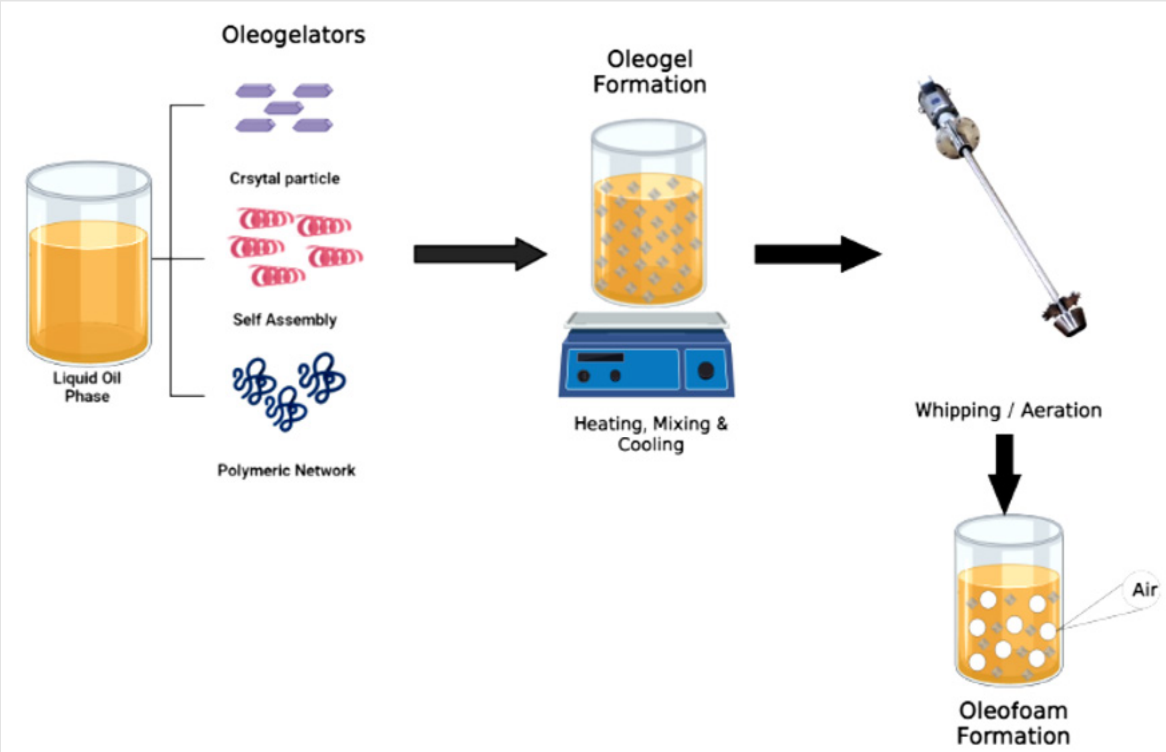

Figure 2: Schematic representation of oleofoams formation from continuous liquid oil phase.

1. Edible oil constituting of good melting edible components is heated above the solubility boundary of mixture followed by cooling. During cooling of edible oil mixture below solubility boundary it leads to crystallization of edible components called oleogels.
2. The second step involves incorporation of air using whipping mechanism results in formation of oleofoams.

Oleogelation is an initial process for development of oleofoams; oleogels are three-dimensional alternative fat supramolecular networks that entraps liquid oil phase which significantly improves the nutritional profile of fat-based products by reducing its saturated fat content but still retains the same calorific value as solid fat. Crystallization properties of oleogels such as size, shape, crystal concentrations, polymorphism, structural properties, viscoelasticity and foamability determine the stability of the oleofoams and its rheology. Incorporation of air bubbles into oleogels is a potential elucidation by decreasing the calorific content retaining the rheological and sensory properties (Salonen, Anniina [6]). From various research works it proves that oleofoams tend to have long-term great stability around and above room temperature with new organoleptic attributes, healthier food ingredient with reduced fat content which are considered as very promising alternative ingredient for food processing industries. It is also identified that oleofoams stability is majorly governed by crystallization properties and also based on contributions from interfaces and bulk. However, a better perceptive on the mechanism of stabilization is still mandatory to facilitate the food processing industry to develop new food system based on oleofoams (Fameau, et al. [7]). There is still dispute on rheological properties of oleofoams, but it appears to be both due to part of the crystals coating the bubbles and to the rheology of the gelled continuous phase in which the bubbles are dispersed. Important key element to be considered before structuring of oleofoams from oleogels, they should behave as viscous dispersions to permit air incorporation once the whipping or mixing process, implying specific rheological behavior of these oleogels (Amani, et al. [8]).

The process of incorporation of gas is the most crucial part: it determines the size of the gas bubbles, the amount of gas holding capacity, the rheology of the liquid continuous phase and the morphology of crystal formation (Binks, et al. [9]). All these defined intermediate parameters responsible for controlling the macroscopic stability and rheological properties of the developed oleofoams. Saremnejad, et al. [10] has developed an aerated reduced fat sauce in a new formulation technique by incorporation of air in the liquid oil phase. The properties of non-aqueous foam were optimized on the effect of whipping speed (3200 rpm); time (10 min) with 10% concentration of mono- & diglycerides. The non-aqueous foam has been used for formulating aerated reduced-fat sauce and compared with commercial full-fat sauce found that formulated sauce shows acceptable stability, thixotropic flow behavior and lightness with stabilized microstructure after six months of storage period. The research findings also proved non-aqueous fat replaced 80% of without compromising its quality characteristics. Metilli, et al. [11] conducted study on highly aerated oleofoams has been obtained by whipping crystallized oleogel prepared using mixture of high oleic sunflower oil and cocoa butter. Results showed that oleofoams obtained from oleogels containing 15 and 22% w/v of cocoa butter displayed overrun of 200% with reduced calorific density and increased elastic & viscous moduli in comparison with oleogel precursor.

It revealed that stabilization of air bubbles and structuring effects has been governed by rearrangement of cocoa butter nano platelets via Pickering mechanisms. The reduction of calorific density developed oleofoams was found to be 1.6 – 2.5 compared to commercial full-fat analogues. Storage studies revealed the stability of oleofoams was up to 3 months at 20°C. Qiu, et al. [12] has prepared hybrid oleofoams with smaller air bubbles and higher stability using medium-long chain diacylglycerol and β-sitosterol in the ratio of 12:8 and 15:5. Pickering mechanism of medium-long chain diacylglycerol crystals formed during gelation induced the network stabilization by providing stearic hindrance over coalescence. The hydrogen bonding of gelators provided synergistic effect for formation and stabilization of air bubbles thus giving stable physical barrier. The development of smaller air bubbles serves as active fillers which lead to enhancement of rigidity to the foam structure. The overrun of medium-long chain diacylglycerol based oleogel was found to be 60.7% and tend to increase with increase in medium-long chain diacylglycerol concentration. Results also show that β-sitosterol has the ability to reduce the clustering of medium-long chain diacylglycerol crystals while medium-long chain diacylglycerol crystals had the impact on crystallization profile of β-sitosterol. The study proved that oleofoams developed using medium-long chain diacylglycerol and β-sitosterol was found to be superior matrixes in retaining bioactive volatile compounds even under stress conditions. Zheng, et al. [13] has fabricated a novel oleofoams by whipping of oleogel constitutes mixture of fatty acids (stearic acid & myristic acid) in sunflower oil. Fatty acids, stearic acid and myristic acids are mixed in different ratios demonstrated to impact gelation properties, crystal morphology and foaming capability of oleogels. The mixture of stearic and myristic acid has been optimized in the ratio of 2:8 and found to produce superior foaming properties and stability due to formation of uniformly distributed and densely packed crystals. Results shows that developed oleofoams exhibited increased overrun of 63.56 ± 2.58% with strong plasticity, improved foaming properties and excellent foam stability. Du, et al. [14] explored the effectiveness of different concentrations of monoglycerides (3,5,7,9 & 11%) has been employed in structuring of oleofoams by whipping monoglycerides based oleogels.

Research revealed that increasing the concentration of monoglycerides promotes tightly packed bubbles with highly concentrated bubble size distributions and stronger interfacial elasticity module. A combination of gelling improvement in oil phase and thick crystal layer around air bubble explains the macro & micro characteristics of oleofoams in close relation with monoglycerides concentration. Result shows that partial coalescence between monoglycerides crystals in oleofoams took place during controlled whipping of oleogels which provided stronger microstructure to foam with desirable foaming properties. It also shows excessive whipping of oleogels leads to destruction of foam and damages the interface between the bubbles. Lei, et al. [15] have designed aerated oleofoams by whipping diacylglycerol stabilized oleogel. The experiment demonstrated that oleogel fabricated with 10 wt% of diacylglycerol exhibited distinctive interfacial crystals around air bubbles thus improves the formation of small crystals and promoted the whipping ability in comparison with 6 wt% fully hydrogenated palm oil based oleogel. The overrun value for 10 wt% diacylglycerol was found to be around 70% which is due to crystal concentration and rheology of oil phase. Liu, et al. [16] investigated two types of vegetable oils (peanut oil & olive oil) containing long-chain triglyceride has been aerated from oleogel state to oleofoams to yield stable oil foams. Crystal formation of vegetable oils has been done through pre-heating of oils to 60°C followed by cooling to -20°C. Developed oleogels was then subjected to aeration using double beater and the influence of time and temperature on foaming properties has been investigated. Optimum overrun foaming yield was found to be ~40% at ≤ -16°C for peanut oil and ~110% at ≤ -12°C for olive oil.

The analysis results revealed that peanut oil foams triglycerides are loosely packed at interface whereas olive oil foams formed with more crystal layers over bubble surfaces. It is also found that these vegetable oil oleofoams are temperature responsive thus melts upon heating around its melting point. Callau, et al. [17] conducted research investigation on the effect of foaming properties on the mixture of fatty acids (Behenic acid & stearic acid) and fatty alcohols (Behenyl alcohol & stearyl alcohol) with sunflower oil as oil phase has been evaluated. Oleogel was prepared by keeping concentration of surfactant constant with varying fatty alcohol and fatty alcohol ratio. The two optimal weight ratios were found to be 7:3 (fatty alcohol) and 8:2 (fatty acid) with improved foam properties such as overrun (42 vol % & 45 vol %), foam firmness and stability. The oleofoams tend to have more concentration of mixed crystals as a result of highest solid fat content and lowest particle size in oleogels. Results revealed that combination of proper ratio of fatty alcohol and fatty acid will promote the oil foaming properties with excellent stability,

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rheology behavior and foamability. Liu, et al. [18] work described the preparation of novel protocol for ultra stable edible oleofoams.

The oleofoams was prepared using mixture of sucrose ester surfactant in vegetable oils containing extra virgin olive oil, high oleic sunflower oil, refined peanut oil and rapeseed oil. Developed protocol involves initial aeration followed by rapid cooling and storage at low temperatures. The resultant oleofoams contain high volume of air fraction with crystalline surfactant around air bubbles. The final oleofoams attains a maximum overrun of 330% with higher stability of more than 6 months and devoid of drainage, disproportionate and coalescence. Grizopoulou, et al. [19] has developed method for spontaneous production of oleofoams through controlled release and entrapment of CO2 gas in water-in-oil emulsions. Development of oleofoams involves two span 60 emulsified water droplets with Na2CO3 as one, the other 10% HCl and caesinate both were mixed with miglyol oil. The reaction of Na2CO3 with HCl acts as micro reactor for controlling pH and subsequent release of CO2. Produced CO2 gas microbubbles were arrested using sodium caesinate thus stabilizing the microfoam structure which expands under increasing pressure resulting into long-term stable foaming oleogels (or) oleofoams. The best results were obtained by equal mixing of acidic and neutral droplets and it also devoid of mechanical operations.

Foam Stabilization Mechanism

The two important parameters governing the stability of oleofoams are the crystal concentrations and the prevalence of crystalline particles, which are directly linked with the solubility boundary. The stabilization mechanisms of oleofoams are demonstrated by the presence of interfacial particles. The stabilization of air bubbles in the oleofoams was majorly carried by the formation of gelation network (oleogels) in the continuous liquid oil phase through non-adsorbed crystals presented in oil. The gel networks developed impended buoyancy driven formation of air bubbles within foam. Research investigation shows that the presence of crystalline particles both at the interface and in the continuous liquid phase stabilizes the oil foam. In Saha, et al. [20] research on oleofoams revealed that there are numerous destabilizing phenomena involved in destruction of gas dispersions therefore it is considered to be associate the bulk properties and interfacial rheological properties that hinders the stabilization mechanisms. The reduction in the surface tension which acts like a packed elastic layer is the initial stabilizing mechanism of crystal layer at the bubble surface thus preventing coalescence and Oswald ripening.

The study also shows that characteristics of bubble surrounded by crystals owe stability to the both bulk and interfacial rheology where as bubble surrounded by liquid oil are only stabilized due to interfacial dilatational rheology of crystal layer. Mishra, et al. [21] predicted the rheological properties of crystallized suspensions of liquid phase lipid system into steady state crystal stabilized micro foam structure. The work also demonstrated that for yield stress dependent foaming of oleogels was higher than gravitational force driven ones thereby no change in phase occurs as well as no change in flow behavior within films separating bubbles. Results also show that without a sufficient contribution of the bulk and interfacial rheological properties the stabilization mechanism of foam against destabilization mechanism is impossible. Apart from various stabilization mechanisms the structuring of oleogel and its solid fat content are the very crucial parameters in the production of oleofoams. The crystal concentration should also maintain high but not too high to efficiently stabilize air bubbles, if not it is unfeasible to produce fluid-like continuous oil phase during emulsification step. The shear rate also plays a significant role in production of oleofoams; too high shear rates causes release of air bubbles whereas too low shear rate results in poor break-up of droplets inside the aqueous phase. In future research works, the relationship between rheological flow properties of oleogel and their respective oleofoams microstructure such as crystal size, shape and concentration throughout the foaming process has to be established.

Mishra, et al. [22] explained new techniques and methodologies to relate rheological and foaming properties of triacylglycerol crystal melt suspensions made up of anhydrous milk fat, palm kernel oil and cocoa butter using in-line ultrasound velocity profiling pressure difference rheometry. The result shows that surface properties of triacylglycerol crystallites determine the formation rate of crystallite clusters. Anhydrous milk fat and cocoa butter mixture constituting more triacylglycerol with unsaturated fatty acids results in rough surfaced crystallites whereas palm kernel oil constituting triacylglycerol with saturated fatty acids results in formation of smooth surfaced crystallites. Difference in foamability properties and foam stabilization mechanism has been demonstrated by the correlation of triacylglycerol crystal-melt suspensions rheological properties and microstructure constituting mixture. In anhydrous milk fat and cocoa butter crystal melt suspensions stabilization of gas bubbles are done by immobilization into continuous gel network while palm kernel oil crystal melt suspensions stabilization of gas bubbles are driven by pickering mechanism and combined network immobilization. Thus helps in understanding relation between crystal mel suspensions microstructure, foamability and rheology to reduce the energy density and volume of saturated fats in lipids.

Mishra, et al. [22] explores the crystallization mechanism and network formation of tripalmitin and monopalmitin at the oil/air interface of middle chain triglyceride. The work presented reveals that tripalmitin formed large, rectangular, polymorphic crystals results in development of deformable networks which leads to stabilization of oleofoams through pickering mechanism. Meanwhile, monopalmitin stabilizes oleofoams by combination of interfacial crystallization and molecular adsorption. The study conducted by Saha, et al. [23]

explains the stability of oleofoams at different time scale by means of crystal layer and interfacial layer behaviors. The experiment has been carried out on isolated single crystal coated air bubbles from an oleofoams at two extreme time scales (~104 s and ~10-3 s). The real time imaging of bubble deformation has been obtained using ultrasound induced oscillation; the experiment result shows that fast deformation of air bubbles in controlled conditions and slow deformation of air bubbles by bubble dissolution. It also revealed that the interfacial layer was affected by dynamics of deformation, includes after complete bubble dissolution, a continuous solid layer remains; after fast, oscillatory deformation of the layer, small crystals are expelled from the layer.

Characterization of oleofoams has included various instrumental analysis such as X-ray diffraction for demonstration of crystal structure in both oleogels and oleofoams (Liu, et al. [18]); optical microscopy for identification of bubble diameter in oleofoams (Liu, et al. [16]); synchrotron X-ray micro computed tomography and radiography to study the microstructure, kinetic behavior and thermodynamic properties of oleofoams (Metilli, et al. [24]; Differential scanning calorimetry used for investigation of crystallization and melting profiles of oleofoams (Zheng, et al. [13]); Differential Interference Contrast Microscopy used in identifying crystal size of oleogel before foaming by photomicrographs (Callau, et al. [17]); FTIR spectroscopy technique has been adopted to characterize the formation of complexes and molecular interaction forces (Liu, et al. [18]); contact angle measurement was performed to evaluate the wettability and hydrophilicity of mixtures in oleofoams formation (Du, et al. [14]); the rheological properties has been carried out using dynamic rheological analysis method to demonstrate the mechanical and flow properties of the oleogel and oleofoams (Lei, et al. [15]). Apart from the mentioned characterization techniques have being used by scientists, a better perceptive of oleofoams could be done using precise characterization techniques such as NMR spectroscopy; Atomic Force Microscopy, Cryo-Scanning Electron Microscopy, Cryo-Transmission Electron Microscopy, Confocal Scanning Laser microscopy, Neutron Tomography, etc.

Metilli, et al. [25] did characterization of 3D microstructure of air-in-oil oleofoams system containing air bubbles stabilized using pickering fat crystals dispersed in continuous oil phase has been demonstrated by non-destructive and non-invasive technique, synchrotron radiation X-ray computed tomography (SR-XCT). Using SR-XCT technique to characterize multiphasic, soft, porous materials are due to its high flux enabling sub-micron resolution, rapid statistical acquisition and penetration of high energy X-rays to produce high resolution imaging and premise to reconstruct the 3D structure of samples. The image processing study revealed the properties of oleofoams in fresh vs heated forms such as bubble shape, size morphology, air phase distribution and thickness of continuous gel phase, whereas time resolved X-ray radiography demonstrated the dynamic changes in 3D microstructure during thermal destabilization, visualization of bubble coalescence and the growth of optically opaque foam samples with respect to time scale. Metilli, et al. [24] has utilized the application of synchrotron X-ray micro-computed tomography and radiography to characterize the microstructure of triglyceride based oleofoams in static and dynamic experiments. It has been used to determine the physical morphology, quantification, thermodynamics and kinetics behavior of oleofoams in their different stages of life cycle (i.e) physical behavior in relevant to aeration and storage conditions. The analysis results revealed that oleofoams showed significant changes in structural morphology such as increase in sphericity and stabilization of air bubbles due to Ostwald ripening of fat crystals in oleogel phase which also significantly decreased the overrun of foam. X-ray radiography has been used to capture the dynamic changes in microstructure of oleofoams for the first time which provided the more accurate temperature needed for mechanical destabilization of oleofoams [26].

Conclusion

We have received a comprehensive understanding of the strategies for making oleofoams from various oleogelators and the application of oleogels in food matrix, as demonstrated by this review. To minimize the level of saturated fatty acids, oleofoams can be added to a variety of foods, including bread and meat products. Overall, the creation of food-grade oleofoam is gaining a lot of interest from academics, but it also has a big impact on the food manufacturing industry. Despite this, the benefits afforded by oleofoam have not yet been completely utilized or commercially viable, owing to a lack of theoretical foundation and experimental efforts. Because the aforementioned issues necessitate extending our knowledge to new depths, future research efforts may be directed in the aforementioned directions. This research will help to increase our understanding of oleofoam and its logical development, as well as broaden the application of oleogel in food matrix and other food-related applications. Oleofoams are considered to be very promising ingredient for the future food processing sector because of its healthier low-fat content, affordability, mouth feel, better texture, long-term stability with improved sensorial properties. Oleofoams will obtain a strong application as fillers, alternative for conventional solid fat, spreads, etc.

Challenges and Future Scope

Despite large number of research works and publication in the field of oleofoams, there is still an enormous gap between commerciality and academic research. Taking the intricacy of pertinent components and of the structures formed as essential part of investigation utilizing the multidisciplinary and multi-scale approach with this complexity is considered to be key element for future developments. It will be possible to manage the breakdown of oleofoam structure, lipolysis rate control, and bio accessibility of bioactive substances in the future by creating custom oleofoam systems. Co-delivery systems require more research, which should be done to show how effective they are in delivering both lipophilic and hydrophilic chemicals. More in vivo research is also required. It is crucial to fully comprehend how these bioactive molecules are absorbed, and this issue needs to be dealt with in the next years. Sensory evaluation will be examined in future studies to ascertain consumer acceptance and preferences for these alternatively designed healthier food products. Identification and utilization of oleogelators from polymers obtained from industrial food waste and byproduct valorization. Development of oleofoam system based on micro and non-structured lipids containing omega-3, omega-6, PUFA, etc compounds. Development of new oleogelation techniques by using various physical and chemical structuring methods will necessitate a deeper comprehension of how oleogels interact with other important food matrix components, such as antioxidants. Further research should concentrate on oxidative stability and sensory characteristics as this area has not been fully investigated. By further processing these ingredients during production, it may be possible to enhance the flavour of products made from oleofoams or cover up their undesirable flavour. It is also important and necessary to include various fields of food science such as nanotechnology, lipid chemistry; food chemistry, food physics, consumer preferences, etc. will be of great potential in addressing the issues related to commercialization of oleogel based systems.

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