REVIEW ARTICLE

European Journal of
Lipid Science and Technology
www.ejlst.com

Oleogelation: From Scientific Feasibility to Applicability in Food Products

Maria Scharfe and Eckhard Flöter*

Oleogels offer the possibility to replace conventional saturated fatty acid (SAFA)-based lipids with a healthier alternative by immobilizing liquid edible oils in a 3D-network which is provided by an oleogelator. Numerous molecules which can structure oils rich in (poly)unsaturated fatty acids have been identified. These differ greatly in their chemical composition, network formation, and interactions and thus macroscopic properties of the respective oleogels. Oleogels have been a focal point of food research for over 20 years, yet product applications are lacking. Hence, the question arises whether the application of oleogels is unfeasible or if science lost sight of its objective. This review aims to assess different structuring systems concerning their availability, their potential for the utilization in food products and, if possible, their prices. Moreover, recent studies comprising the application of oleogels in food products are reviewed with special emphasis on the state and the function of the lipid phase during processing and in the final product. Therefore, the physical properties and preparation methods of different oleogels need to be considered in connection with the respective food application. Finally, it is discussed whether the application of oleogels is justified in these products and advantageous in comparison to liquid oil.
***Practical Applications*: A diet rich in mono-and polyunsaturated fatty acids which make up the majority of liquid edible oils lowers the risk to suffer from cardiovascular diseases. Unfortunately, these oils cannot provide texture to food products in their native state. Oleogelation has the potential to deliver the solid structure necessary for numerous food products by transferring an oil rich in essential fatty acids into a solid-like structure. Besides, the nutritional value of these oils remains practically unchanged. Although oleogelation has been the objective of various research groups for more than 20 years, product applications are scarce. This review aims to stimulate the mindfulness of research concerning the successful application of oleogels in food products. This hopefully enables a better connection between science and industry.**

1. Introduction

The fatty acid (FA) composition of triacylglycerols (TAGs) determines the physical state of edible fats and oils at room temperature. As a matter of principle, a higher number of double bonds favors a liquid nature while a high level of saturated FAs and a long hydrocarbon carbon chain is linked to a solid or semi-solid state. Solidification of TAGs is the result of their assembly into crystalline nanoplatelets (CNPs), which are the foundation of structured lipid phases. As CNPs stack and/or aggregate to form larger crystalline entities, liquid TAGs are immobilized within the 3D network. In food products, these structured lipid phases meet diverse functional needs on a macroscopic and microscopic scale. Among others, these are stabilization of surfaces, macroscopic hardness, and other rheological properties as well as disintegration characteristics and melting behavior including organoleptic sensations.[1,2]

High consumption of saturated fatty acids (SAFAs) in the daily diet has been linked to impair cardiovascular health for decades. Yet, it was revealed recently that a high intake of SAFAs could not directly be related to an increased risk to suffer from coronary heart diseases (CHD). However, replacing SAFA with polyunsaturated fatty acids (PUFAs) can be connected to a significantly reduced risk of CHD incidents.[3,4] Hence, a diet which favors mono- or poly-unsaturated fatty acids over SAFAs is recommended.[5] Since many adults in the United States are not consuming sufficient amounts of ω-3-PUFAs to meet the recommendations given by, for example, World Health Organization (WHO) and Food and Agriculture Organization (FAO), action must be taken to increase their concentration in food products.[6,7]

Unfortunately, plant-based oils rich in monounsaturated fatty acid (MUFAs) and PUFAs do not provide the structure which is essential for many food products due to their liquid nature at ambient temperature. Additionally, potential alternatives to the established structuring route—saturated fats—have to satisfy needs which are specifically tailored to meet the requirements of the individual food product. Consequently, eliminating

M. Scharfe, Prof. E. Flöter
Department of Food Processing
Technical University Berlin
Seestr. 13, Berlin 13353, Germany
E-mail: maria.scharfe@tu-berlin.de

DOI: 10.1002/ejlt.202000213

European Journal of Lipid Science and Technology
www.ejlst.com

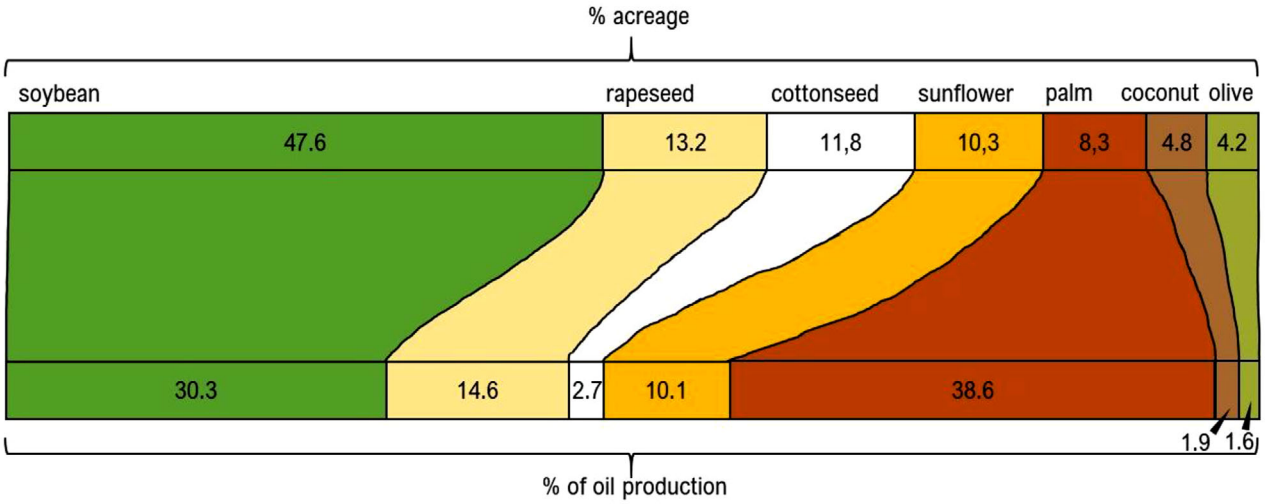

Figure 1. Relation of acreage percentage (total area of oil crops mentioned) to the percentage of oil production volume (total production volume of oil crops mentioned). Adapted with permission.[13]

SAFAs from functional fat ingredients such as shortenings or confectionary fats is desirable but remains a challenge for the food industry.

Currently, the TAGs used to design functional fat phases mainly originating from palm oil and other hydrogenated plant oils. In general, hydrogenation was stigmatized since partially hydrogenated fats contain significant amounts of trans fatty acids (TFA). These are known to increase low-density lipoprotein while simultaneously lowering high-density lipoprotein.[8] Accordingly, a high TFA intake increases the risk to suffer from CHD by 21%.[9] Public health authorities consequently recommend limiting TFA consumption to less than 1% of the total nutritional energy.[5,10] However, in 2010, the global TFA-energy contribution was estimated to be 1.4% (ranging between 0.2% and 6.5%) with North America, Brazil, Egypt, and Pakistan having the highest consumption per capita.[11] Although the ban of TFA was already initiated in the 1990s, various food products such as convenience products, baked goods, or fried foods still contain elevated levels of trans fatty acids. Diligent efforts have been made to decrease the concentration of TFA in these products by varying standard recipes and developing suitable quality guidelines.[12] A study report of the *Bundesinstitut für Risikobewertung (BfR)* from 2013 stated that at most 1.46% of the daily energy consumption in Germany can be traced back to TFA (on average 0.66%).[10] Even though the reduction of TFA in food products has been carried out reasonably well, alternatives to hydrogenated oils are still needed.

Palm oil production, on the other hand, has experienced a substantial boom since the beginning of the 1980s, as initially Malaysia and later Indonesia increased production capacities dramatically. Among established oil crops, palm trees deliver by far the highest yield per hectare acreage (**Figure 1**, Ø 3.1 t ha^{-1}). It needs to be mentioned that yield levels of up 8 t ha^{-1} are achievable with best agronomic practices. In combination with low production costs, this renders palm oil the most significant edible oil with 73.3 Mio t or 38.6% of the global production in 2018.[13]

Palm oil comprises roughly 50% SAFAs (primarily palmitic acid 16:0) and 50% MUFAs and PUFAs (mostly oleic acid (18:1)

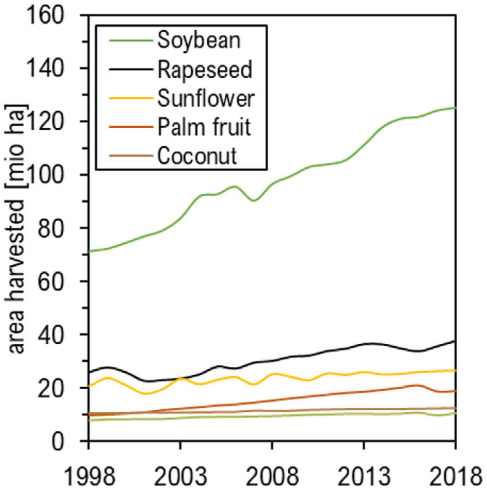

Figure 2. Development of acreage of different oil crops from 1998–2018.

and linoleic acid (18:2). Via fractionation, various high- and low-melting palm oil fractions are obtained. These fractions and their combinations are the origins of a multitude of functional fat phases delivering desired product properties such as hardness or melting temperature. Mid fractions of palm oil, for example, can be blended to imitate the unique melting profile of cocoa butter. Considering the low production price, high oil yield, availability, and unique FA composition, palm oil has a distinctive position on the global market. Moreover, the expected global population growth necessitates the cultivation of the most productive crops.

From an environmental perspective, the position of palm oil is debatable. It has been under criticism for deforestation of natural or sustainably used rainforest.[14] Deforestation decreases biodiversity and causes CO_2 emissions. Irrespective of the method of deforestation, the CO_2-binding capacity of palm oil plantations is much lower than of rainforest (approximately 1/3), which results in an inferior CO_2 balance.[15,16] However, from **Figure 2**, it appears that the cultivated area for soybeans is the largest among

oil crops. Of course, the most substantial acreage for soybeans is not the tropical zones but the temperate zones of North and South America. However, the soybean acreage of Brazil alone exceeds the global acreage of palm oil plantations significantly (≈21 Mio ha PO, ≈36 Mio ha soybean in Brazil,.[13,17]

Many organizations ranging from the Round Table for Sustainable Palm Oil (RSPO) over the Malaysian Palm Oil Board (MPOB) to NGOs like WWF are committed to improving the sustainability of palm oil. Yet, the consumers' perception of palm oil is at least controversial. The combination of partly flawed information and the growing environmental and ecological awareness are conducive to sustain this critical view in industrialized countries.[18,19] Hence, the increasing demand for healthy, organic, sustainable, and regional food products has led to the impetus to develop products comprising alternatives to current structuring routes based on crystalline triglycerides, which mainly originate from palm oil or other tropical oils. The entrapment of liquid oils into non-TAG network structures is a very promising route to deliver higher amounts of PUFAs in food products. As a consequence, the application of regionally produced oils such as canola or sunflower oil is promoted.

Essentially, providing structure to liquid edible oils can be realized through 1) crystalline particles, 2) self-assembled networks, 3) polymer networks, and 4) emulsions. The vast number and diversity of publications concerning the topic of oleo-/organogelation (>2.500) indicate that many gelling agents have been identified in the past 20 years. Still, the number of product launches is fairly meagre considering the global scientific effort documented in more than 8000 patents.

This paper aims to provide a critical review of the status quo in oleogelation with emphasis on crucial targets of oleogel use, product applications, and gelator production volumes and costs. Therefore, selected structuring systems are presented briefly, and the most significant drawbacks of each structuring route are discussed concerning their availability, price, and applicability. Moreover, publications featuring product applications of oleogels are reviewed. The functionality of the lipid phase in the product will be considered as well as its physical state during processing and in the final product.

2. Oleogels

Giving a holistic definition of a gel has been discussed controversially ever since the existence of gels was recognized. It is however generally acknowledged that a gel exhibits a solid-like rheological behavior and contains a continuous liquid phase which is immobilized by a structure. This structure or network is provided by a gelling agent with limited solubility in the continuous phase. This vague definition indicates the complexity of the nature of gels. Similar to that, numerous descriptions of oleo- or organogels are considered.

In this study, oleogels are considered to be semi-solid materials which display a linear visco-elastic region. **Figure 3** shows oleogel structuring mechanisms classified into the building blocks which provide structure to the continuous phase. However, for this work, the distinction from traditionally structured lipid phases is that the non-polar liquid is entrapped by a hydrophobic non-TAG-based structure.

Figure 3. Methods of oil structuring classified by the mechanism which provides the solid network structure. Blue circle: Reproduced with permission.[42] Copyright 2018, Elsevier. Green circle: Reproduced with permission.[101] Copyright 2009, Elsevier. Yellow circle: Reproduced with permission.[112] Copyright 2009, Elsevier.

The ongoing research activities reveal new structuring systems to date, among which variations of wax compositions and ethylcellulose have been considered to be the most promising to find access to food manufacturing processes. However, the combination of phytosterols and γ-oryzanol remains of interest since this combination can lower blood cholesterol levels and prevent aortic fatty streaks.[20–22] Mono- and diglycerides of fatty acids can be produced in large quantities as well and entrap liquid oil in 3D networks similar to saturated TAGs. Since their functionality as structurant is related to high levels of SAFAs, monoglycerides offer essentially no benefit over the conventional triglyceride structuring route.

These examples already illustrate that successful replacement of conventional semi-solid lipid phases is far from trivial due to the need to satisfy both functional and economic demands. According to Co and Marangoni[23] and Bot and Flöter[24,25] reasonable candidates for oil structuring should preferentially:

- be food grade
- provide a functional structure to edible oil
- be affordable
- not interfere with other ingredients in a product
- be versatile, for example, offer the possibility to design specific product properties such as melting temperature
- ensure similar taste and mouthfeel

This list of conditions aims to deliver the ideal system and it is obvious that meeting all criteria simultaneously is inconceivable. In addition, it lacks a crucial parameter for successful product applications: consumer acceptance. Consumer acceptance remains crucial and cannot be achieved if the replacement does not offer a similar sensory sensation or other exceptional

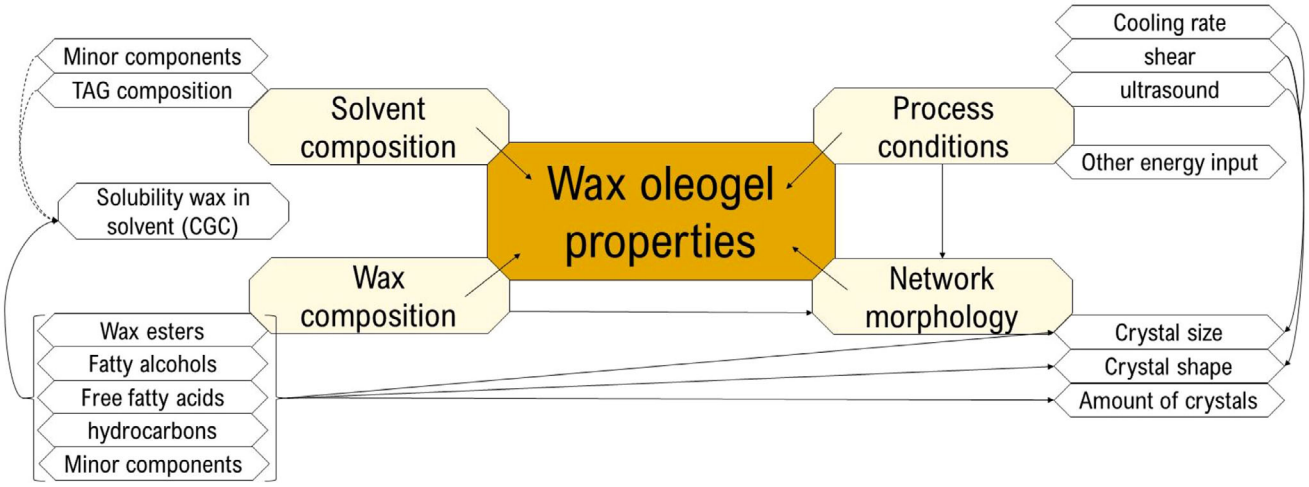

Figure 4. Factors affecting wax oleogel properties.

benefits. Consequently, the last two conditions listed above are most critical and yet most difficult to accomplish since nearly all oleogel systems rather disintegrate than melt while consumed. As a result, the sensation perceived by the consumer is different.

Regarding the scientific output in the field of oleogelation, the direction of the research seems questionable. The benefits of studies which illustrate that oleogels can be generated by a combination of known structurants with oils different than those utilized in previous studies are limited. It would be conducive if the research would unravel underlying principles instead of being phenomenological. The considerations outlined above and illustrated in the following are hence meant to stimulate the mindfulness in oleogelation research.

3. Ethylcellulose

Ethylcellulose (EC) is a food-grade polymer composed of β-D-glucose monomers, at which ethyl groups partly substitute free hydroxyl groups. The desired degree of substitution (DS) for oleogelation ranges between 2.2 and 2.8 (45-53%). This degree of substitution enables EC to be soluble in solvents with a low polarity such as edible oils and organic solvents such as aliphatic alcohols.[26]

Dow Chemicals and Ashland, two US-based companies, produce significant volumes of ethylcellulose. The primary starting material for EC production is wood pulp with at least 86% α-cellulose content. The substitution can be realized in a batch or semi-continuous process using ethyl chloride after the cellulose has been alkalified.[27] The global production of wood pulp (184 Mio t in 2017) primarily aims to satisfy the demand for paper products.[28] The production of ethylcellulose from wood pulp is hence of minor importance. Additionally, the wood pulp market prices experienced a substantial increase over the past decade from approximately \$520 t^{-1} in October 2009 to \$870 t^{-1} in October 2019.[29]

However, municipal solid wastes (MSW), more specifically from paper wastes, offer the possibility to produce tremendous amounts of EC. The MSW fractions of office paper, for example, contain 87% cellulose. Moreover, food waste covers varying quantities of cellulose too, accounting for around 50% of the residue on average.[30] Potential production volumes and prices of ethylcellulose are thus hard to estimate. In an optimistic attempt, one could summate recovered paper (waste paper), other fiber pulp and the wood pulp, as they all contain high levels of cellulose. The global production of the aforementioned products reached 415 Mio t in 2016.[31] Assuming that 0.1% (0.415 Mio t) was used to produce EC, a cellulose content in the pulp products of 87% and an yield of 1.25–1.3 t EC per t cellulose,[27] the annual production can be estimated to 0.45–0.47 Mio t. This would yield, assuming a 10% structurant composition, potentially 5 Mio t of structured fat phases annually.

EC can structure edible oil primarily via interactions of unsubstituted hydroxyl groups which form inter- and intramolecular hydrogen bonds between the backbones of the polymer strands.[32] Moreover, EC-based oleogels are found to have a bicontinuous porous structure.[33]

EC oleogel hardness increases with 1) the EC concentration, 2) the degree of unsaturation of the continuous phase (edible oil), or 3) the molecular weight of EC.[33,34] The first effect can be linked to a more solid structure in the gel which also results in a reduction in pore size. A greater iodine value (IV) of the continuous phase reduces the pore size as well.[33] It was argued that the lower molar volume of TAGs with a high degree of unsaturation decreases polymer strand separation and thus enables more tie points in the network.[32] Interestingly, the pore size does not seem to be affected by the molecular weight of EC. The increase in hardness was in this case attributed to longer polymer chains which facilitate a greater number of intermolecular junction zones.[35] Besides, a synergistic effect of EC in monoglyceride oleogels was reported when EC was used below its critical aggregation concentration (CGC).[36] The gels showed improved viscoelastic properties, lower oil loss during storage, and delayed sub-α to β polymorphic transition of the monoglycerides. This might be the result of an increased number of hydrogen bonds formed in the presence of EC. Surprisingly, the addition of small amounts of glycerol monooleate to EC oleogels had the opposite effect. The storage modulus (G′), which indicates the degree of cross-linking in a gel network, was much lower than in the pure

EC oleogel.[35] In contrast, sorbitan monostearate seems to aid cross-linking and thus G′ was higher than in the pure EC oleogel.

However, ethylcellulose must be heated above the glass transition temperature (T_g) to induce gelation upon cooling. T_g depends on the molecular weight of the polymer and was found to be typically between 135–145 °C.[37] The minimum amount of EC needed to structure either soybean or canola oil was found to be 4 and 6 wt%, respectively.[38] That might indicate that EC is less soluble in triglyceride-oils with a higher degree of unsaturation (higher IV). The higher IV can also be related to increased relative permittivities. However, these differences in critical concentration may also be attributed to the presence of polar minor oil components (PCs), which interact with the oleogelator.[39,40] Thus, the changes would arise from changes in the interactions of the structuring elements instead of changes in the solubility. For example, a linear decrease of sol–gel phase transition temperature was found in sterol/sterol-ester oleogels when the concentration of polar components was increased. The decline may be the result of interactions between PCs and the sterols and higher solvent viscosity and thus a lower diffusion rate of the sterols.[41] Moreover, the authors reported a different appearance of the elements of scaffolding (tube bundles) in the presence and absence of polar components. Polar components hence likely interact with the unsubstituted hydroxyl groups of EC, thus hampering network formation and altering network structure. These changes could also affect the macroscopic properties of oleogels, such as hardness and critical gelling concentration. Thus, both the TAG oil composition and the presence of minor components, corresponding to oil quality, do modify the properties of oleogels. Since the oils used in the studies mentioned above were not characterized comprehensively, the effect of PCs in these studies remains indistinct.

The intense heating process during EC-oleogel preparation inherently bears the risk of the formation of oxidation products. The progress of the oil deterioration is a function of the starting material and process execution. Although the role of minor oil components and deterioration products has been recognized, a coherent approach to elucidate their effect on microscopic and macroscopic oleogel properties is missing in recent literature. To adequately disentangle this problem, the contributions of the continuous phase (TAG composition) and dissolved polar minor components must be studied separately.[41]

However, in a recent study, it was found that network appearance and macroscopic properties of EC oleogels changed significantly upon selective oil purification.[42] The removal of minor components led to softer gels with smaller, elongated pores. The authors claimed that the EC solubility was decreased upon purification due to lower solvent polarity. Unfortunately, EC solubility was not determined. Nevertheless, AFM data revealed that on extended oil purification, the EC network backbone thinned down and pore sizes decreased.[42] The conclusion that smaller pores are not necessarily associated with stronger gels conflicts with earlier work. Zetzl et al. stated that smaller pores result in stronger gels due to the increased number of intermolecular junction zones.[33] This indicates that smaller pores cannot be associated with stronger gels in general.

Anyhow, ethylcellulose has been an interesting structurant for edible applications expressed by the vast number of publications and patents. Moreover, EC oleogels may also be used in non-food applications such as the delivery of water-insoluble drugs and nutrients and vegetable-oil-based lubricants.[43,44] In Section 10, fat functionality for different structurant systems is discussed in detail.

4. Waxes

Waxes are organic compounds which are lipophilic and soluble in organic non-polar solvents. Their composition is chemically diverse but characteristically comprises long alkyl chains (>16 carbon molecules) which may contain unsaturated bonds. These chains may have several functional groups such as carboxyl, hydroxyl, ketones, aldehydes, and esters. Typically, natural waxes consist of combinations of wax esters (fatty acid + fatty alcohol), free fatty acids, fatty alcohols, and hydrocarbons. The mixture of these components, as well as their individual composition, alkyl chain length, and the number of unsaturated bonds, defines the physical characteristics of the wax. Moreover, minor wax components such as sterol esters and esters of pentacyclic triterpenoids and alcohols may impact the characteristics as (**Figure 4**). Natural waxes commonly melt between 50–80 °C and are thus solid at ambient temperature, which relates to their biological function.

It is generally assumed that wax esters—the predominant constituent in most waxes—are very poorly absorbed by mammals (<50%). This is due to, i.a., the low bile salt and colipase concentration in the intestinal and gallbladder of mammals, which does not promote sufficient enzyme activity to separate the FAs and FAOHs from the ester backbone.[45,46] This implies that waxes per se do not contribute to the nutritional value of a food product. However, recent studies have shown that marine waxes in the oil extracted from *Calanus finmarchicus* (>86% of FAs present as wax esters) can be absorbed by humans.[47] This oil contains considerable amounts of the essential fatty acids docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA), which are known to lower the blood pressure and blood triglyceride levels and thus the risk of CHD.

Waxes of commercial significance include bees-, carnauba, candelilla, rice bran, sunflower, and sugarcane waxes. The fact that some waxes are byproducts renders them economically more attractive than other structuring systems. Rice bran (RBX) and sunflower wax (SFX), for example, may be recovered from waste streams during oil refining while sugarcane wax (SCX) can be obtained from the dry filter cake after juice purification. On the other hand, beeswax (BWX) makes up the skeletal structure of honeycombs and carnauba (CRX), and candelilla (CLX) wax can be harvested from the leaves of *Copernicia cerifera* C. Martius (CRX) and *Euphorbia cerifera* and *Euphorbia antisyphilitica* (CLX), respectively.

Waxes of different origin show great variations in their ability to gel plant oils because of their network structure which is i.a. related to their composition (**Figure 5**). A comprehensive approach to relate organogel properties to the wax composition, the solvent properties, the manufacturing conditions, and the crystal morphology is lacking until now. In a recent study, a positive correlation of levels of HC, FFA, FAOH, and WE with oleogel strength expressed as storage modulus (G'_{LVR}) was formulated.[48] However, hardness seemed to decrease when more FAOHs were present. Surprisingly, the negative effect of FAOHs on oleogel strength was found to be considerable while the contribution of WEs and FFAs is stated to be only marginal.[48] On the other

European Journal of Lipid Science and Technology
www.ejlst.com

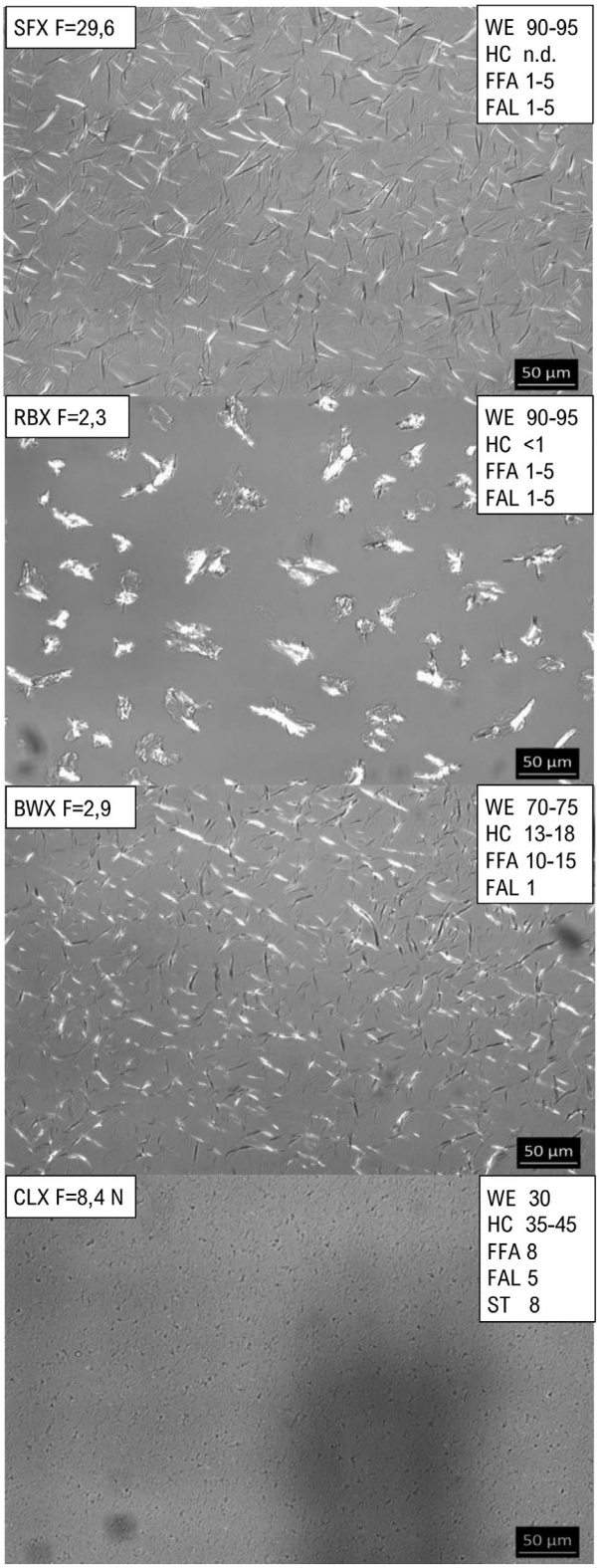

Figure 5. Optical micrographs taken at the Department of Food Process Engineering of 4% wax oleogels in natural canola oil, from top to bottom: sunflower wax, rice bran wax, beeswax, candelilla wax; top left corner: F—hardness of oleogels; top right corner: wax composition provided by manufacturer (KahlWax).

hand, hydrocarbons, which were only present in considerable amounts in CLX and BWX, appeared to contribute more to gel structure than WEs and FFAs. Interestingly, RBX and SFX showed a very similar overall composition (% of WE, HC, FFA, and FAOH) but the G'_{LVR} was eight times higher for SFX than for RBX. Moreover, the CGC of RBX was 5%, while it was only 1% for SFX.[48] The differences in G'_{LVR} and CGC correspond to the different crystal morphologies of RBX and SFX (Figure 5). In polarized light microscopic images, RBX displays irregularly shaped crystals of approximately 20–60 µm; while in SFX-based oleogels, a space-filling network of needle-like crystals is observed. This visual assessment correlates well with the respective oil-binding potential, gel strength, and lower CGC (Figure 5). On a molecular scale, these morphological variations might be due to longer hydrocarbon chains of the FA and FAOH moieties in WEs of RBX (mainly C_{20-24} and C_{24-30}). Longer chains show greater intermolecular dispersion forces and are thus able to pack tighter and have a higher melting point and lower solubility. However, RBX has a greater disparity in alkyl chain length of WEs than SFX, which possibly influences crystal growth. As a result, growth of SFX crystals might be favored in one direction while the growth of RBX crystals appears to be more uniform in all directions. Besides the wax type and composition, the morphology of crystal networks in wax oleogels substantially depends on the manufacturing process, which in itself should be a function of the composition. This is well illustrated by the results obtained for candelilla wax (CWX) oleogels. Under constant shearing during a complete cooling cycle, fairly weaker gels were produced, although small micro-platelets were present. These are in general associated with a better oil binding capacity.[49] Interestingly, shearing until just above the apparent crystallization of CLX resulted in much harder gels and a higher storage modulus despite similar micro-platelet sizes. The authors concluded that molecular alignment and network interactions must be improved by this procedure. One should not forget that this is the basis for a random influence of the arbitrary selection of the standard gel production procedure on the evaluation of different structuring systems. Additionally, minor oil components and oxidation reaction products are able to modify the appearance of wax crystals.[209]

As pointed out above, the availability and affordability of a structuring system are key parameters for its application potential. To this end, **Table 1** lists potential production volumes and prices of the aforementioned wax species. Since the CGC can vary significantly with wax and solvent composition as explained above, potential oleogel volumes were estimated conservatively using the respective highest CGC found in the literature. It should be recognized that trustworthy data on global production volumes and prices of waxes is rare. This is due to the poor transparency of the market and the dependence of the production on external factors. In this aspect, beeswax is an exception since global production volumes are offered annually by the FAO.[13]

In contrast, the potential production volume of SCX was calculated based on its respective core product. In 2017, approximately 1900 Mio t of sugarcane were harvested worldwide. SCX can be extracted from the dry filter cake, which makes up 3.3% (60 Mio t) of the total amount of sugarcane.[50] Assuming an average wax content of 9% in the cake, 5.4 Mio t of crude SCX may be available per year.[51] Crude SCX has a distinctive odor which is not acceptable for food products. Therefore, refining is necessary and

Table 1. Production volumes, CGC, and prices of commercially available wax types.

Parameter	SFX	RBX	CLX	CRX	BWX	SCX
Production volume [1000 t]	1–5[a)]	>50[a)]	1–2[a)]	16–18[a)]	67[b)]	3800[c)]
					10–15 food[a)]	
CGC [wt%]	0.5–1	1–5	0.75–2	3–5	1–3	3
Oleogel volume [Mio t]	10	1	0.05	0.3	0.3	126
Wax price [$1000/t]	—	—	—	5[d)]	3–7[e)]	—

[a)] Ref. [210]; [b)] Ref. [13]; [c)] Estimated based on sugarcane production worldwide; [d)] Ref. [65]; [e)] Range producer price in Mexico, Turkey, Argentina, Spain, Kenya.[64]

the loss during this process step may be as high as 30%.[52] This would equal a potential production of 3.8 Mio t of refined sugar cane wax per year (Table 1).

The most reasonable process to extract rice bran wax (RBX) is during rice bran oil (RBO) purification. According to the FAO, 782 Mio t of rice (paddy) were harvested in 2019.[13] Assuming that about 8% of bran are removed during rice polishing, 62.5 Mio t rice bran would be available.[53] Rice bran typically contains 15–30% lipids[54,55] and 0.4–1.5% wax.[53] Consequently, 9.5–18.8 Mio t of crude RBO could be produced. Crude RBO comprises 3–4% waxes on average, but waxy types can contain up to 8%.[56] This would enable an annual production of about 0.4 Mio t RBX (assuming production of 14.1 Mio t crude RBO). The actual RBX production, however, was >50 000 t recently[210] because only 1.2 Mio t rice bran oil were produced from rice bran in 2017 while the majority of bran is sold as a low-cost animal feed.[57] The estimation of RBX production has shown that actual and potential production diverge widely. This underlines again that waxes may be economically more attractive than other structuring systems.

The potential amount of oleogel was calculated for each wax species as a function of its respective critical gelation concentration (CGC). Commonly, the CGC is the minimal concentration at which the mixture of wax and solvent does not flow when turned upside down at a certain temperature (20 °C). It needs to be mentioned at this point that the CGC strongly depends on the wax composition, its minor components, the composition of the solvent, and the manufacturing process of the gel.[58–60] For example, CLX can structure high oleic sunflower oil at a concentration as low as 0.75%,[61] while it was reported in other studies that 2% was needed to gel refined soybean, olive respectively canola oil.[61–63] Additionally, it has been reported that CGC of several types of RBXs varied between 0.5 and 5%.[58] These differences in CGC are most likely related to different RBX compositions. This illustrates not only the complexity of the gelling behavior of waxes but also the necessity to perform an in-depth characterization of waxes and solvents to obtain comparable results. Consequently, the volumes stated in are certainly too optimistic because CGCs do not necessarily represent a wax dosage that warrants food functionality. Anyhow, relative application potential might be covered adequately.

However, waxes show great potential to substitute fats with high levels of saturated fatty acids in food products due to their chemical diversity. They enable the production of oleogels with distinct thermal and rheological properties. Wax oleogels might be tailored through the mixing of various wax types, and less practical though the utilization of different edible oils, so that potentially melting properties of complex systems such as confectionery products might be mimicked.[66] Nevertheless, a waxy mouthfeel is probable in high-fat products such as shortenings. However, sensory evaluations of baked goods such as cookies have shown that the utilization of wax-based oleogels can even result in a greater acceptance when compared to commercial bakery shortening.[67]

Regarding the production volumes and prices, in future scenarios, the market will certainly be subject to changes. For example, 80 000–100 000 t of sunflower wax could be produced annually.[210] Most of the wax is currently recovered from filters during the refining of crude sunflower oil. However, sunflower seed hulls contain a considerable amount of wax (up to 3%[68]), while the wax content in crude sunflower oil is much lower (about 0.14%[69]). The combustion of the hulls generates heat which is used during sunflower oil production. Since the wax impairs the combustion process, the extraction would be advantageous. The potential production of additional 60 000–80 000 of SFX[210] due to wax extraction from hulls appears small compared to the potential determination of SCX volumes discussed above. Nevertheless, the production of wax as a side stream from major commodities like sunflower oil, cane sugar, or rice represents a very promising sourcing opportunity.

5. Sterol/Sterol-Ester

In search of new structuring systems for oleogelation, a few binary systems such as the combination of FAs and FAOHs have been identified. The combination of phytosterols and sterol esters, however, is unique since the behavior of the mixture cannot be predicted from the behavior of its individual components. This paragraph will first provide an introduction of the individual components, including their possible production volumes before the mechanism of oleogelation, and the properties of the gels will be discussed.

5.1. γ-Oryzanol

Oryzanol is not a single component, but a mixture of ferulate esters of triterpene alcohols and phytosterols.[70] Yet, it was reported that 80% of the blend consists of cycloartenyl ferulate, 24-methylenecycloartanyl ferulate, and campesteryl ferulate.[71]

Several positive effects are associated with the consumption of γ-oryzanol, such as lowering plasma and serum cholesterol, reducing cholesterol absorption, and increasing the muscular mass.[72–75]

Oryzanol can be extracted directly from rice bran with either organic solvents or supercritical CO_2 (SCFE). Moreover, oryzanol can be recovered during rice bran oil refining. In **Table 2**, potential production volumes of oryzanol extracted from rice bran are shown. These are calculated based on an annual rice production of 782 Mio t (2018) assuming that during milling, 8% bran (≈62.5 Mio t) is removed from the paddy rice.[13,53] It was reported that rice bran has reached its production potential[76] but only a small fraction is used to extract rice bran oil and its valuable byproducts such as waxes and oryzanol. Crude rice bran oil contains 1.5–2.0% oryzanol and about 8% waxes. The soap stock which is obtained after neutralization during the refining

Table 2. Oryzanol production from rice (production 782 Mio t),[13] results in 62.5 Mio t rice bran (assuming a rice bran content of 8 %,[53]), amount oleogel calculated based on 4 wt% sterols on oil of which 60% is oryzanol; price per t oleogel based on an estimated sunflower oil price of \$900 t^{-1} (December 2019, https://fred.stlouisfed.org/series/PSUNOUSDM).

Extraction technique	Yield [mg g^{-1} rice bran]	Potential production [Mio t]	Price[a] [\$1000 t^{-1}]	Potential amount of oleogel [Mio t]	Price per t oleogel [\$ t^{-1}]
Solvent	1.68 ± 0.02[b]	0.105	14.6–102	4.3	1230–3330
SCFE	5.39 ± 0.20[c]	0.337	219–1096	13.8	6130–27180

[a] Ref. [79] [b] Hexane:isopropanol (1:1), 60°C, 60 min;[78] [c] CO_2, 68.9 kPa, 50 °C, 25 min.[78]

of crude rice bran oil offers an effective way to extract oryzanol. The process includes low-temperature distillation followed by several hydrolyzations and precipitation and filtration treatments (see ref. [77] for more details).

However, actual production volumes of oryzanol from rice bran or rice bran oil refining are lacking, and extraction yields and estimated production prices of oryzanol are quite variable (Table 2). If oryzanol would be gained as a byproduct from the neutralization waste during rice bran oil refining, costs might be reduced. The recovery of oryzanol during rice bran oil refining is reasonable and maximizes product output from rice bran. In contrast to rice bran, rice bran oil production is far from reaching its full potential (1.2 Mio t/9.5–12.5 Mio t in 2017, FAO new food balances).

5.2. β-Sitosterol and Other Phytosterols

β-sitosterol represents the biggest fraction of plant sterols commonly found in plant oils, about 40–80%.[54] Like other phytosterols, β-sitosterol is extracted from side-product streams of commercial oil production. Precisely, sterols can be recovered from condensate obtained during deodorization. While the distillate constitutes only 0.3–0.5% of the total processed oil volume, it can contain 8–20% phytosterols depending on the type of oil used. Moreover, sterols can be extracted from tall oil, a by-product of the wood pulp manufacturing process. After distillation, the tall oil pitch contains approximately 5–15% phytosterols, of which 40–65% are β-sitosterol.[80] According to FAO, the annual production of chemical wood pulp was 1464 Mio t in 2018.[81] Typically, 30–50 kg tall oil per t wood pulp can be recovered.[82] In a conservative approach, the potential production volume of mixed phytosterols with a high content of β-sitosterol from tall oil can thus be estimated to be 219 630 t (based on 30 kg tall oil per t wood pulp, 5% sterol content). Nevertheless, tall oil production is far from reaching its full potential with an annual production of about 1.2 Mio t,[83] which facilitates for an annual production of 60 000 t. Unfortunately, data on actual production volumes and prices of mixed sterols is lacking.

The consumption of β-sitosterol offers similar positive effects on human health as it has been discussed for oryzanol in the previous section. Additionally, both are widely used as a dietary supplement. As the market for health-boosting supplements is steadily growing, it can be expected that sales are equally increasing, which in turn would raise production volumes while simultaneously production costs decline.

Ever since the sterol/sterol-ester system was discovered, other phytosterols were screened for their ability to form oleogels with oryzanol.[84] Ergosterol, stigmasterol, cholesterol, and cholestanol were identified to form oleogels with oryzanol in edible oils.[85] Cholesterol is the only phytosterol which is available in large quantities. However, cholesterol might never be utilized in oleogel food products due to its strong negative perception by consumers, although the correlation of cholesterol consumption and blood cholesterol levels remains controversial.

5.3. Gelation of the Binary System

Oryzanol self-assembles into nanoscale hollow tubes if combined with other phytosterols such as β-sitosterol and cholesterol.[86] The gels' appearance varies from slightly hazy or transparent due to the size of the primary building blocks and the presence of material not included in the tubules. Depending on the type of oil and its composition, 2–4 wt% of sterol/sterol ester mixture is needed to form a gel at 5 °C. At low gelator concentration and quiescent conditions, gelling is rather irregular. Since it was derived from X-ray scattering that tubule nucleation and growth occurs within minutes, the limiting process is believed to be tube aggregation.[87,88]

Infrared spectroscopy and molecular dynamic simulations revealed the occurrence of a hydrogen bond between the hydroxyl group of the phytosterol and the carbonyl group or oryzanol.[87,89] This hydrogen bond is considered to be crucial for the stacking of the molecules in a tilted way and thus the formation of a helical tubule (**Figure 6**). Consequently, a 1:1 molar ratio of oryzanol:phytosterol (60:40 weight ratio in case sitosterol is used) is preferable. The weight ratio of sterol:sterol ester needs to be adjusted to maintain a 1:1 molar ratio when other sterols such as cholesterol are utilized. ($M_{cholesterol}$ ≈386 g mol^{-1}, $M_{sitosterol}$ ≈414 g mol^{-1}).

Interestingly, the gel hardness and its dissolution temperature vary for oleogels based on different phytosterols. These properties decrease in the order stigmasterol > sitosterol > cholesterol.[85] Although the stacking of the oryzanol is similar with different phytosterols of the hydrogen bond, the tube dimensions varied between 6.7–8.0 nm with a wall thickness of 0.8–1.2 nm.[85,89] Consequently, interactions of the primary building blocks could vary when different phytosterols are used. This hypothesis is supported by the changes in oleogel dissolution temperature: cholesterol ≈72 °C, sitosterol ≈84 °C, and stigmasterol ≈92 °C for gels with a structurant concentration of 16 wt%.[85] Moreover, the ferulic acid moiety of oryzanol which protrudes out of the tube into the surrounding is able to enhance the stability of the same by forming noncovalent interactions within one helix.[89] However, in the presence of another tube, the same interactions, in particular van der Waals interactions and π–π contacts, are responsible for tube–tube interactions

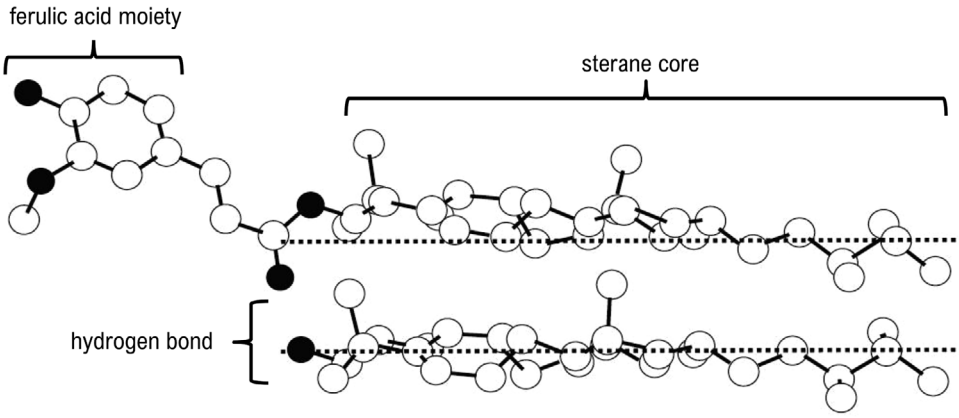

Figure 6. Hypothetical stacking of oryzanol with sitosterol, ferulic acid moiety protrudes into the surrounding, hypothetical parallel stacking indicated by dotted lines. Reproduced with permission.[25] Copyright 2018, Elsevier.

and thus the gelation of the continuous phase. Obviously, the number of interaction points is limited by the number of sterols in the gel, and thus there is a shift from intra- to inter-tube interactions when tubes stick together. It was reported recently that inter-tube interactions may be altered in the presence of polar minor components, which results in a modified network appearance on a microscopic scale and different macroscopic properties such as gel strength.[41] Moreover, the tubular structure is disturbed in the presence of water since the formation of β-sitosterol monohydrate crystals is favored.[87,90,91] Consequently, the oil immobilizing structure is partly lost in, for example, emulsions. However, lowering the water activity to values below 0.9 has been proven to be an effective tool to maintain the delicate structure formed by sitosterol and oryzanol.[92] Finally, the oleogel properties can be modified by the type of solvent used.[41,92,93] In contrast to EC oleogels, the firmness decreases with the number of unsaturations in the oil. This decrease seems to be related to oil viscosity, which declines in the same way.[209]

6. Others

6.1. 12-Hydroxystearic Acid

Over the past decades, numerous other oil structuring systems have been discovered. The aim of this paper is not to cover all of them but to evaluate the potential of the most promising. Nevertheless, two other oleogelators will be briefly discussed in this section.

12-Hydroxystearic acid (12-HSA) is obtained via catalytic hydration of castor oil. During this process, other reactions such as dehydration reactions occur, which lead to the formation of stearic acid. Consequently, the typical composition of commercial 12-HSA is a mixture of 84–85% 12-HSA, 8.3–9.5 % stearic acid, and about 5% triglycerides.[94] Castor oil is obtained from the seeds of the castor oil plant *Ricinus communis*. The oil content of castor seeds varies greatly depending on cultivation conditions but was found to be between 37–61%.[95] Due to the high oil content in seeds, 1.250–2.500 L oil can be obtained per hectare.[96] In 2018, 1.4 Mio t of castor seeds were harvested, the majority (86%) in India, Brazil (5%), and China (7%).[13] However, most of the oil is used as a lubricant or after hydrogenation in polishes, waxes, and cosmetics.

A hydrogen bond which is formed between the hydroxyl groups enables the self-assembling of 12-HSA in edible oils. As a result, twisted helical strands of crystalline 12-HSA are formed.[97,98] These fibers further form a 3D network via van der Waals interactions, which immobilizes the continuous liquid phase. It was shown that the nature of the solvent affects these interactions and thus the appearance of the network.[99,100] Consequently, the critical gelling concentration of 12-HSA varies but was found to be relatively low in edible oils (1%, e.g., canola oil).[101,102]

Although 12-HSA is not yet approved by the FDA for food products, it was utilized in model chocolate fillings comprising interesterified hydrogenated palm oil (IHPO) and canola oil (40:60 w/w) to impede oil migration.[103] Unfortunately, the oil migration in oleogel samples was found to be higher than in the control sample. It was hypothesized that 12-HSA interferes with the network formation of IHPO, thus changing the packing and morphology and consequently impairing the oil binding capacity and increasing oil mobility. Nevertheless, it was shown that 12-HSA oleogels could be a promising tool for the controlled release of neutraceuticals in tablets[104] or even injectable implants.[105]

6.2. Proteins

An alternative approach for oil structuring which has attracted considerable attention over the past years is the utilization of proteins. This method, however, remains challenging since proteins are predominantly hydrophilic, although some amino acids have hydrophobic side chains. Consequently, a supporting structure which entraps liquid oil cannot be formed directly. One approach to structure edible oil with proteins is the conversion of a protein-stabilized oil-in-water emulsion into a protein oleogel (emulsion-templated approach[106]). To this end, the protein stabilizing the interface of the primary o/w emulsion is cross-linked to form a stable interfacial layer. The cross-linking can be chemical, thermal, or enzymatic. Subsequently, the continuous water phase can be reduced or removed by applying heat which results in compact gels that are high internal phase emulsions (HIPEs)

with an oil content of >90%. Spray-drying offers another possibility to convert the primary o/w emulsion.[107,108] Consequently, oily powders are obtained which offer conventional advantages over the concentrated HIPEs. Similar to the slow evaporation, the fast water evaporation and high temperatures during spray drying promotes the formation of oxidation products and needs to be considered. However, the method seems to be suitable to skip the initial process of cross-linking the protein at the interface, in case of soy protein isolate.[108] Because of the high energy input during the (spray) drying process, a flexible and rigid interface is necessary to prevent coalescence and oil leakage and ensure the stability of the final emulsion. The addition of polysaccharides such as carrageenan[109] and xanthan[110] to the continuous water phase can improve the interface elasticity and stability due to co-adsorption.

Another strategy to structure edible oil with proteins was suggested by de Vries et al.[111] In contrast to the emulsion-templated approach, it is based on the denaturation and consequently alteration of protein functionality. In their native state, proteins are water soluble with their hydrophobic domains embedded on the inside of the folded structure. Due to denaturation which primary alters the non-covalent intramolecular bonds, the protein unfolds, hydrophobic areas are exposed, and thus protein solubility changes. This enables for a gradual exchange of the polar solvent water with less polar solvents such as acetone and subsequently edible oils. The method of denaturation (thermally, pH, the addition of salt), the concentration of protein (protein aggregates or network), and further processing of the network such as freeze-drying determine the final oleogel properties. Oleogels obtained by this procedure are thus by definition actual oleogels, while in HIPEs the oil is the dispersed phase. Detailed information about the different methods for protein oleogel preparation, their properties, and modification can be found elsewhere.[109–117]

Proteins which have been utilized to structure edible oil include whey protein isolate,[111,112,114,116–119] β-lactoglobulin,[106,107] soy protein isolate,[109,113] and gelatin.[110] The functionality of these proteins depends on their composition but is often hard to estimate since they comprise a mixture of different individual proteins (except β-lactoglobulin). Moreover, particular functionalities are required depending on the protein oleogel preparation method, the processing, and functionality in the final product. For the emulsion-templated approach, proteins have to be surface-active and coagulate. This can be realized by thermal treatment or precipitation due to a pH close to the isoelectric point. However, modification of proteins through hydrolysis is a powerful tool to tailor protein functionalities and thus might facilitate the production of proteins with improved oleogelling properties.

One of the key advantages of proteins for oleogelation is their availability and price when compared to other structurants. The market for whey proteins, for example, has experienced an ongoing increase over the past years due to a boost in, especially, sports nutrition, which was approximately 6% between 2011 and 2015.[120] Concentrated whey protein products (WPC) are classified by their protein content: WPC50-89, WPC80, and whey protein isolate (WPI, >95% protein). In 2017, the market volume of WPC50-89 and WPI was estimated at 380 000 and 80 000 t, respectively,[121] while the prices for 1 metric tonne were between \$4000–5000 (WPC 50–89) and \$5.800 (WPI).[122] Needless to mention that a similar trend is to be expected for soy protein, although most of the soy meal from which proteins can be extracted is still used for animal feed.

This paper primarily aims to focus on the availability of the structurants and the functionality of the fat which ought to be replaced by an oleogel in the final product and during processing. Concerning nutritional value and labeling, proteins are very promising candidates for oil structuring. However, the methods discussed in the previous section are rather costly and intricate and the final oleogel properties are in some cases hard to predict. Nevertheless, it is another young, promising research field with the significant advantage that the structurants are available in large quantities. Protein sources which have been used include whey protein,[111,112,114] pure β-lactoglobulin,[106] soy protein,[109,113] and gelatin.[110] Certainly, other proteins such as pea protein or egg isolates will be studied soon as well. Moreover, mixing proteins from different sources as well as modification utilizing hydrolysis imparts their functional properties and allows for the tailoring of desired characteristics of oleogels.

To validate the applicability of protein oleogels in food products, margarine and pork fat were substituted in cookies and frankfurter sausages, respectively.[115] Here, oleogels gels were prepared by coagulation and subsequent solvent exchange. Although the protein oleogels were not further specified, the results suggest proof of principle for the application in shortbread dough and meat batter. Moreover, sensory tests with a small panel revealed no undue differences in product structure.

In the case of the emulsion-templated approach, the critical step is the redissolution of the powder during or before further processing. This step enables tailoring the properties of the oleogel but can also cause destabilization. It was reported for spray-dried oil powders that the application of shear greater than the Laplace pressure of the droplets resulted in droplet breakup.[108]

Both methods of preparation comprise various difficulties which still restrict their commercial use. The preparation of HIPE emulsion gels or powders always includes a two-step process. However, both steps—emulsification and drying—are continuous processes which can be operated on a large scale. Moreover, the utilization of ready-to-use oil powders which are tailored for specific applications is conceivable. Nevertheless, the extend of oxidation reactions during the drying process is still unclear, but studies comprising the application of freeze-dried protein agglomerates have shown a positive correlation of protein oxidation with water content during storage at elevated temperatures.[117,119]

The solvent exchange method, on the other hand, offers the possibility to produce prefabricated protein aggregates or networks. On the downside, the utilization of an intermediate solvent is less favorable. At this time, there is much room for improving preparation methods as well as understanding network interactions. Nevertheless, proteins, due to their versatility, availability, and nutritional value, offer a great possibility to be used for oil structuring. Moreover, consumer acceptance is unmatched and the use of plant proteins is in line with the growing consumer demand for vegetarian or vegan food products. Continuing investigations on protein modifications and functionality and utilization in food products will reveal further limitations and advantages of these oleogels.

Table 3. Estimated production volumes and prices for selected oil structuring agents, assuming a sunflower oil price of \$900 t^{-1} (December 2019).

Structuring material	Production volume [Mio t]	Price [\$ t^{-1}]	Min. %wt for oil structuring	Amount of structured oil [Mio t]	Price per t structured oil [\$ t^{-1}]
Palm oil	71.4[a)]	550[a)] (06.2020)	Straight	71.4	550
PPP from palm oil	5.7[b)]	750[b)]	3–4	142.7–190.3	896–903
EC	0.45–0.47[c)]	1000[d)]	3–4	11.3–15.7	903–913
SFX	0001–0005[a)]	1000[d)]	0.5–1.0	0.2–0.5	900.5–901
RBX	0.4[c)]	1000[d)]	1–5	8–40	901–905
SCX	3.8[a)]	1000[d)]	3	126.7	903
β-sitosterol/ γ-oryzanol	0.2[c)] 0.11–0.34[c)]	1000[d)] 3330[c)]	2–4 (40:60 mass ratio)	4.6–28.3	1361–1919

[a)] Actual, see respective paragraph in Section 4; [b)] Assuming 8% tripalmitate (PPP) in PO, additional costs of double dry fractionation estimated \$200 t^{-1}; [c)] Potential, see respective chapter for details; [d)] Guessed to calculate the price per t structured oil, the actual price is likely much higher.

7. Intermediate Summary

The pressure in finding healthier alternatives for solid lipid phases which mainly consist of saturated fatty acids has led to the discovery of numerous oil gelling systems. Their network structures and interactions, as well as their rheological, physical, and chemical properties differ greatly. However, the aforementioned can be modified by the gelator composition, concentration, the production process, and type and composition of the continuous phase. Nevertheless, none of the systems discussed will match semi-solid lipid phases based on SAFAs in every aspect. Besides, prices per tonne structured oil exceed those of palm oil and even dry fractionated tripalmitin (**Table 3**). It needs to be mentioned that in Table 3, several prices were estimated to allow for the price calculation. Actual prices of waxes, for example, are likely much higher as it is indicated in Table 1 for beeswax production price (3000–7000 \$ t^{-1}) and carnauba wax market price (5000 \$ t^{-1}, 2010). However, prices are likely to decrease once production volumes increase and manufacturing processes are integrated into existing production lines (e.g., wax extraction from sunflower seed hull). Additionally, the health benefits associated with the consumption of (poly)unsaturated fatty acids outweigh the additional costs.

Thus, the utilization of oleogels in selected food products is reasonable but the functionality, state, and amount of the lipid phase in the product need to be considered. For example, the utilization of oleogels in food products where the lipid phase is, for example, responsible for a particular melting sensation is difficult since oleogels rather disintegrate than melt while eaten. However, a partial substitution or the development of new products (e.g., heat resistant chocolate) may be possible.

The following chapter will review recent publications with emphasis on the state of the lipid phase during processing and in the product since that is considered crucial for successful product development.

8. Digestion

According to the WHO non-communicable diseases account for the death of 41 Mio people each year (or 71% of all deaths) of which 17.9 Mio can be associated with cardiovascular diseases.[123] Behavioral risk factors such as nutrition and physical activity play a crucial role in the development of cardiovascular diseases.[124] It has been proven that replacing SAFAs with PUFAs (n-3, EPA, DHA) reduces serum cholesterol as well as the LDL/HDL ratio, but did not result in an overall increase of cholesterol or blood pressure and thus a higher risk to develop CHD.[3] Moreover, it was shown that the reduction in blood cholesterol is similarly successful when PUFAs are incorporated in a complex food matrix such as patés and sausages.[125] Briefly, lipases have to break down the TAGs into FAs and mono- and diglycerides in the small intestine to enable for the absorption of valuable MUFAs and PUFAs (occurs to some extent in the mouth and stomach as well). Diffusion into the intestinal epithelial cells is then realized via diffusion from micelles of aggregated lipid metabolism products.

Consequently, to provide lipids from oleogels the gel network has to be broken down to release the TAGs. Oleogels have been used for controlled delivery of pharmaceuticals since it was shown that the release of lipophilic substances such as ibuprofen can be retarded when they are incorporated into a hydrophobic network.[104,126,127] However, release and bioavailability of TAGs from oleogels is much more complicated when incorporated into a food matrix. Here, physiochemical properties such as interfacial phenomena play a significant role as well.[90,128] In general, due to the restriction of TAGs in the oleogel network, the lipase activity is impeded and a retarded release of FAs was observed for different structuring systems.[90,104]

This is in line with a study where a high fat-diet comprising wax oleogels decreased lipid digestibility in rats.[129] In contrast, utilizing wax oleogels in sponge cake bread lead to an increased in vitro starch digestion which might be associated with an increase in short-range crystallized starch structures.[130] Nevertheless, the variation in digestibility of macronutrients is likely to be individual for each oleogelator. Moreover, it is generally known that the digestion of a substance depends on the matrix (food product) it is incorporated in. This indicates the complexity of the issue and to this day only a few studies are addressing it. Within the scope of this work, the release from different food matrices cannot be discussed but there are some excellent reviews concerning this topic.[131–134]

However, the question of greater significance (in terms of legislation) is the metabolism of the network providing molecules. Oleogelators comprise a great variety of hydrophobic molecule classes. Therefore, their absorption in the intestine and subsequent metabolism displays a great variance. Furthermore, most

Table 4. Overview of the legislation situation of selected oleogelators molecules in the United States and Europe.

Oleogelator	USA			Europe		
	GRAS	Purpose	ADI	E number	Purpose	ADI
12-Hydroxy stearic acid	—	—	—	—	—	—
Beeswax	GRAS[a)]	Chewing gum, confections and frostings, hard candy, soft candy, others	No ADI, depends on the product	E 901	Glazing agent, surface treatment of fruits, food supplements, color carrier	None[154]
Candelilla wax	GRAS[a)]	Lubricant, surface-finishing agent, chewing gum, hard candy	None	E 902	Glazing agent	None[135]
Carnauba wax	GRAS[a)]	Anticaking agent, surface-finishing agent, baked goods, chewing gum, processed fruits, soft candy, sauces	None	E 903	Glazing agent	None[136] 7 mg kg^{-1} (JECFA)
Ethylcellulose	GRAS[b)]	Grain products, vegetables, fruits, milk products, nuts and seeds, fats and oils, sugar, beverages	No ADI, depends on the product	E 462	Binder, filler	None[155]
Mono-diglycerides	GRAS[a)]	Emulsifier or emulsifier salt, flavor enhancer, flavoring agent or adjuvant, lubricant or release agent, masticatory substance, stabilizer or thickener, surface-active agent, texturizer	No ADI, depends on the product	E 471	Emulsifier, stabilizer	None (currently re-evaluating)[137]
Phytosterols/-esters	GRAS[a)]	Meat, poultry, fish, dried beans, pea, nuts and seeds, grain products, fruit and vegetable products, oils, dressings, sugars, sweets, beverages	2–3 g	None, novel food[c]	Dressings, mayonnaise, milk-type products, spreadable fats	3 g[139] 40 mg kg^{-1} (JECFA)
Rice bran wax	GRAS[b)]	Candy, fresh fruits and vegetables, chewing gum, snack bars	No ADI, depends on the product	908 (INS)	—	—

[a)] Ref. [212]; [b)] Ref. [213]; [c)] Ref. [214].

of the structurants mentioned in **Table 4** are mixtures of different types of molecules. This section will thus only provide very basic information about the digestion of oleogelators.

Before new molecules are deregulated for food use, they have to undergo clinical studies unless their absorption is believed to be similar substances which are already authorized (e.g., waxes of different origins). Thus, valuable information about the absorption and digestion of oleogelators can be derived from legislation reports provided by the officials (WHO, FAO, EFSA, FDA).

8.1. Digestion of Oleogelators

Waxes mainly consist of a mixture of wax esters, long-chain hydrocarbons, free fatty acids, and fatty alcohol (see Section 4 for details). It has been reported that intact wax esters are poorly absorbable and are mostly excreted in feces.[46] For a successful uptake, the fatty alcohols and acids must be released from the ester backbone.[46,135] However, only small fractions of wax esters are hydrolyzed since humans lack bile salts which are segregated in fish and seabirds to breakdown wax esters.[46]

However, waxes also comprise different concentrations of free long-chain fatty alcohols and acids. Their uptake was proven to decrease with chain length and hydrophobicity. Nevertheless, very-long-chain fatty alcohols and possibly FAs were reported to lower LDL and raise HDL in humans.[46]

The absorption and metabolism of isolated alkanes were found to be less than 25% in rats.[46,135,136] Once absorbed, they undergo extensive metabolism in the liver to acidic compounds which are then eliminated in the urine.[135]

Interestingly, for rats who were fed a high-fat diet, it was shown that RBX oleogels decreased adipose tissue accumulation, TAG levels in serum and liver, and cholesterol in the liver when compared to beef and margarine.[129] Since the human diet always contained modest levels of waxes from seeds, nuts, cereal grains, and honeycombs, their consumption is considered to be safe.

It was reported that cellulose is not absorbed intact in the gastrointestinal tract but is partly fermented by the microbiota.[137] Similarly, it was concluded that modified cellulose (methyl-, ethyl-,...) is excreted mainly via the feces (>90%), while small amounts of metabolites can be found in the urine.[137,138]

Plant sterols (PS) like β-sitosterol are structurally similar to cholesterol and thus potentially influence the absorption, metabolism, and excretion of the same.[139] Indeed, in the presence of phytosterols, the blood cholesterol levels are lowered since they inhibit the intestinal absorption of cholesterol.[140] However, in contrast to cholesterol (55–60%), the absorption rate of PS mixtures from the gastrointestinal tract is much lower

(about 5%, depending on the mixture).[139–142] Absorbed phytosterols/stanols are excreted as such or converted to bile acids in the liver and subsequently excreted.[139] Phytosterol/phytosterol ester emulsions (o/w, 10/90) showed slower lipolysis probably due to restriction of TAGs in the gel structure (substrate limitation)[90] or adsorption of lipase on the hydrophobic surface of the elements of scaffolding (enzyme restriction).[143] Moreover, oxidation of PS must be prevented since it results in a loss of their LDL-cholesterol-lowering effect.[144]

It is generally accepted that phytosterol esters such as γ-oryzanol are—similar to plant sterols—poorly absorbed from the intestinal tract.[145,146] Once absorbed, the sterol esters are distributed into a variety of tissues and subsequently metabolized to, i.a., ferulic acid and phytosterols.[147] Recent studies suggest that hydrolysis can also happen in the gastrointestinal tract resulting in a similar cholesterol-lowering effect like that of phytosterols. Additionally, the ferulic acid moiety inhibits an enzyme involved in the production of cholesterol in the liver.[148]

Thus, the official panels concluded that phytosterols and their esters can be used safely to provide an "additional" cholesterol-lowering effect in hypercholesterolemic patients.[149] Moreover, a study with phytosterol margarine (8.6 g sterols per day) showed that 4 weeks of consumption had no significant effect on the fecal bacterial profile of humans.[150,151] However, it was found that food products comprising increased levels of phytosterols/-stanols can lower the absorption of β-carotene (by 20%) and α-tocopherol (levels were still within normal range).[152,153]

9. Legislation

Next to the economic restraint discussed in the sections above, oleogelators are considered direct food additives and thus need approval from the respective state authorities. In Europe, new food additives are approved according to the regulation (EC) No 1333/2008 (16.12.2008) and assigned an E number to inform consumers. Approval is only granted if the additive is:

- not a risk to human health (based on scientific evidence)
- technologically required
- not misleading the consumer

The E number system has been internationally adopted and extended by the Codex Alimentarius Commission (international numbering system for food additives, INS) which provides a collection of recognized standards for good food practice, safety and transparency (founded by the FAO and joined by WHO). FAO and WHO further release the Joint FAO-WHO Expert Committee (JECFA) Report on food additives regularly.

Before approval, the European Food Safety Authority (EFSA) evaluates the health and safety of a new food additive or reassesses existing additives based on new scientific insights. The approval is usually granted for certain food applications mostly including an acceptable daily intake (ADI). This assessment is commonly based on current research deducting long-term feeding studies on animals and/or humans. Hence, the approval of a completely new food additive is a tedious procedure.

Additionally, the EU stipulated the Novel Food legislation (according to EC Nr. 1829/2003) for foods which comprise:

- a new or modified molecular structure
- microorganisms, fungi, algae or extracts of the aforementioned
- novel plants, animals, or their extracts
- a novel process which causes a change in food structure, composition, or their metabolism.

Applicants have to send a proposal to the EU commission (which can then consult the EFSA), including details about the foods' composition, production processes, and scientific evidence which confirms that the product does not pose any danger to human health. Once approval is granted, the novel food is added to a union list. However, approval and admission procedure are lengthy if the novel food is significantly different from an existing food product or food ingredient. It needs to be mentioned that in the EU, any health claims associated with a food product or ingredient must be approved separately according to Regulation EC 1924/2006.

In the United States, food additives are approved and regulated by the FDA unless they are listed as "generally recognized as safe" (GRAS). GRAS approval is issued by experts and only for the intended use according to the Federal Food, Drug, and Cosmetic Act (FFDCA). In contrast to the E number system, food additives in the USA are listed using their Chemical Abstracts Number (CAS) and FDA regulation number (according to the US Code of Federal Regulations).

Authorization procedure can internationally be conducted by the official commissions and committees, countries, or any other interested party (e.g., companies).

Table 4 shows the current legislation on food additives used for oleogelation in scientific publications. Most of the substances are accepted for utilization in specific food products. The upper limit is thus often determined by the application: for example, the use of waxes as glazing agents. Other waxes such as rice bran and sunflower wax (limited to cosmetic use) can be expected to receive approval for food use based on data and feeding studies for other approved plant waxes since their composition is very similar. However, when used for oil structuring, the oleogelators have to pass legislation processes of the FDA and EFSA (and Novel Food) again. Additional feeding studies might have to be conducted during this procedure depending on the amount of structurant in the final product. Nevertheless, most feeding studies conduct trials with exposures much higher than the estimated intended consumption. For example, in toxicological studies of plant waxes, the no-observed-adverse-effect levels (NOALs) of wax constituents were 10–50 times higher than the conservative approach suggested by the EFSA (22 mg kg^{-1} day^{-1}). The limitations given by the authorities are based on the metabolism of the respective component among other things. Consequently, the following chapter will give a brief overview of the digestion of oleogelators. For more details, the evaluations on food additives published by the EFSA or FDA can be considered.

10. Food Applications

Edible oleogels can improve the nutritional value of food products since they offer the possibility to increase the concentration of essential, unsaturated fatty acids in edible structured lipid phases. To this end, plant oils which are typically liquid at room

Table 5. Selection of oleogel food applications.

Category	Fat function	Product/problem	Oleogel system	Refs.
Confectionary products	Snap, appearance, melting sensation	Heat resistant chocolate	EC	[156,158–161]
		Reduced-fat chocolate	EC	[162]
		Oil migration/confectionary fillings	12-HSA	[103,163,164]
			Sterol/sterol-ester	[157]
			Wax	[66]
Meat products	Snap, texture	Sausages (frankfurter-, breakfast-, Bologna-type), hamburger	Sterol/sterol-ester	[165–168]
			EC, wax	[38,168–174]
			Pork skin emulsion	[175]
	Texture, spreadability	Pâté	EC, wax	[176,177]
			EC+ MAG	[178]
Margarine+ spreads	Emulsion stabilization, hardness, melting properties, spreadability	Margarine/spreads	Wax	[179–182]
Shortening for pastries	Prevents adherence of gluten and starch, air cell stabilization, mouthfeel, flavor release	Cookies	EC, wax	[183–187]
		(Gluten-free) cake	Wax	[130,174,185]
			EC	[173]
Dairy products	Richness, creaminess, scoopability, stabilization	Ice cream	Sterol/sterol-ester	[188–190]
			Wax	[191]
	Richness	Yoghurt	Sterol/sterol-ester	[192]
	Richness, spreadability	Cream cheese	Wax	[193,194]

temperature are immobilized by a 3D network. This way, they may be used as solid fat replacers in numerous products. Additionally, they have the potential to resolve issues occurring in existing products, for example, oil migration and recrystallization in chocolate. Finally, production processes might be simplified and new products could emerge, such as heat-resistant chocolate (HRC).[156]

In this section, product applications of oleogels will be discussed with emphasis on the functionality of the fat in the original product. Considering the production process, it is crucial to understand at which stage the rheological properties of the lipid phase (fat or oleogel) matter and how it has to be incorporated into the product matrix. These parameters significantly limit the applicability of oleogel structuring systems, for example, if high shear is applied during processing. It also needs to be evaluated whether or not the utilization of an oleogel is reasonable, or if liquid oils in their native state are sufficient for the particular application.

A vast number of research articles have dealt with food applications of oleogels primarily as fat replacers or immobilizing agents (**Table 5**). Products with a high solid fat content such as shortenings or chocolate are usually preferred. Table 5 indicates the great variety of products in terms of fat functionality in the original product. The physical state of the fat during the process and in the final product is a crucial parameter for the applicability of oleogels. For example, in ice cream, the fat has to be liquid during homogenization (60–70 °C) to form small droplets, while it has to solidify during ripening (≈4 °C) to form a supportive network in this complex food matrix. In contrast, solid fat globules are favored from the start in meat batters before they are cooked to create the appropriate microstructure delivering the expected snap and texture in sausages.[38]

10.1. Confectionary Products

In chocolate production, the fat does not only determine the appearance, snap, and melting sensation of the final product, but also targets the actual process conditions. During crystallization, temperature control must be precise to avoid crystallization of cocoa butter into undesired polymorphs. Before that, during the conching of the cocoa mass (60–65 °C for milk chocolate), the fat needs to be molten to ensure coating of the particles. Moreover, the liquid state of the fat lowers the viscosity during conching which improves the mobility of ingredients in the mass, enables for the discharge of undesired flavors, and prevents particle aggregation.

Consequently, oleogels which aim to replace or substitute cocoa butter in chocolate-like applications have to meet a series of extremely specific demands during the process and in the final product. Until today, oleogels did not replace cocoa butter successfully. Instead, their utilization was studied in filled confectionaries,[66,103,157] heat-resistant chocolate,[156,158–161] and fat-reduced chocolate.[162]

The latter publication dealt with the use of EC (0.05 wt%) in model chocolate systems containing cocoa butter equivalents

(CBE), lecithin, and sugar to improve the coating of the dispersed phase and thus prevent particle aggregation. The authors reported that owing to the presence of EC, the viscosity of the mixture (at 40 °C) was significantly reduced, which could aid particle coating and flavor development.[162] Unfortunately, this study does neither include storage tests to ensure that EC stays at the particle surface nor are the results directly transferable to an actual chocolate mixture. Moreover, it remains vague how the mixture behaves upon cooling and crystallization. In other studies, however, EC was utilized in realistic chocolate mixtures to develop heat-resistant chocolate.[156,158–161,195] The authors found that EC is able to form hydrogen bonds with sucrose which results in the formation of a network.[160] This outcome is rather unexpected since EC was believed to immobilize the cocoa butter at elevated temperatures. Instead, the interactions between EC and sucrose not only provided mechanical strength to the chocolate but also entrapped the oil. Thus, the EC oleogel acts in synergy with the sugar particles. Large deformation tests showed that HRC still had a hardness of 18 N at 40 °C.[159] Unfortunately, the authors did not provide the melting profile of HRC, but at 80 °C, samples were still not entirely molten, indicating that sensory properties of HRC are unlikely to satisfy consumer demands. Evaluating this product with caution, it is fair to assume that an oleogel with a solid fat phase exists at low temperatures. When heated, the cocoa butter is melting and the structure transforms into an oleogel immobilizing the liquid cocoa butter. The stability of these products is hence to be expected to coincide with the disintegration temperature of EC oleogels or even the sugar EC network.

Anyhow, oil loss in chocolate samples after 10 days at 40 °C was significantly reduced in the presence of EC, which indicates that the sugar-EC network could impede recrystallization and fat bloom formation of cocoa butter as well. Erratic storage conditions (temperature) are believed to be one of the key factors affecting fat bloom development in chocolate products.[196] In filled confectionaries, recrystallization is additionally promoted by oil migration into the outer chocolate layer. More precisely, cocoa butter TAGs dissolve in the liquid portion of the filling and consequently migrate to the surface via diffusion and/or capillary forces where they recrystallize.

- Therefore,[157] immobilization of oil through gelation might impede oil migration. Different approaches were suggested to prove this hypothesis:gelation of the filling
- gelation of the chocolate layer
- formation of a distinct oleogel barrier

In another study, oleogels made of γ-oryzanol/β-sitosterol were used to monitor oil migration in nougat pralines during 24 weeks at 10, 18, and 28 °C.[157] The authors included the three approaches mentioned above and used a gel inclusion level of 2.5% in the filling and the chocolate cover while the barrier layer made up 14% of the total sample. Moreover, they used structurant levels of either 10% or 25% and determined relative liquid oil level in the chocolate via differential scanning calorimetry (DSC). Not surprisingly, at 10 °C, no oil migration was detectable while it was highest at 28 °C. It is interesting to note that at 25% structurant concentration and 28 °C oil migration was most impeded when the gel was used in the chocolate layer. In contrast, the three-layer system, as well as the sample with gelled chocolate, showed higher or similar oil migration at 18 °C and 10% oleogelator compared to the reference. When the filling was gelled, oil migration was successfully suppressed even at lower sterol+sterol-ester concentration. The results showed that γ-oryzanol/β-sitosterol oleogels can effectively hamper oil migration and that the additional oil introduced with the gel does not promote incremental migration of oil. Thus, saturated fatty acids can be reduced and at the results obtained at elevated temperatures might enable praline storage in tropical climes.

Similar results were reported by 66 for mixtures of palm oil and beeswax/rice bran oil oleogels in model fillings containing hazelnut mass and sugar. They substituted PO with organogels comprising different concentrations of beeswax. At a substitution level of 17% and either 2.5%, 3.0%, or 3.5% structurant concentration samples showed a significantly lower oil loss than the reference while simultaneously having similar rheological properties (storage modulus). This implies that oil migration in the final products might be suppressed as well. Moreover, their solid fat content counterfeited the reference filling nearly perfectly at body temperature (≈2%), suggesting that the addition of wax oleogel did not negatively affect the sensory properties. Nevertheless, it is questionable whether the SFC testing method which is designed for crystalline triacylglycerols produces reliable results for crystalline waxes and thus sensory tests are indispensable. Unfortunately, the study did neither include long-term storage of the fillings (>5 days) nor the application of the same in a genuine product. However, the results suggest that wax-based oleogels can substitute PO in chocolate-like products and thus enable for SAFA reduction.

10.2. Meat Products

In comminuted meat products, the fat globule size, as well as the relation of fat to protein, is a major factor defining the final product structure. In order to obtain a stable batter, the myosin protein needs to form a network which supports the sizeable animal fat globules (<100 μm).[197] Due to the lower temperatures (≈8–12 °C) during the mincing process, the beef fat remains semi-solid. Anyhow, the globules are ruptured because of the intense mechanical treatment. As a result, a broad fat globule size distribution is observable in the final product which is responsible for the snap but also the soft texture of the sausage.[38] Early studies have shown that the substitution of meat fat with edible oils caused a substantial increase in firmness and chewiness of sausages.[197–199] This is due to the presence of almost exclusively small droplets (<20 μm) with narrow size distribution and thus a much larger fat surface area which enables enhanced protein adhesion at the interface resulting in a more homogeneous and stiffer protein network filled with fat globules.[38] Consequently, the sensory properties of products based on ungelled vegetable oil are unlikely to meet the consumers' expectations.

Oleogels aiming to replace animal fat should thus be added to the batter in the solid-state to hamper the excessive droplet breakup during mincing. The resulting fat globule sizes have to be similar to the original to deliver products with nutritionally improved fatty acid profile but unchanged structural properties.

This has been illustrated for ethylcellulose oleogels substituting the animal fat in cooked sausages (frankfurters).[38,158] In this study, 17.5 wt% of canola oil, beef fat, or an oleogel (10% EC 10 cP, canola oil) were used in lean meat (7.5% fat) to produce finely comminuted meat batters and consequently frankfurter sausages. The sausages with EC oleogel showed similar hardness and chewiness to the beef fat product while samples with pure canola oil were significantly harder.

Interestingly, sausages containing EC oleogel had a much smaller average fat globule size (median 7 μm) than the regular sample (median 25 μm) and fewer globules exceeding 20 μm (10% compared to 30%). As a result, the authors hypothesize that globules between 9–24 μm must have the greatest effect on texture rather than fat particles of >100 μm. It might also be possible that protein network formation is suppressed in oleogel samples considering that oil entrapped in discrete pockets within the EC network. Moreover, the beef fat is—unlike the oleogel—liquid during the cooking process (72 °C), which enables more protein to adsorb at the oil droplet surface and form intermolecular interactions. As a result, there could be greater changes in the protein network formation during cooking. This might explain the similar textural properties of oleogel and regular sausages although their fat globules sizes differ significantly. However, there is no data available on the interaction of proteins at the EC oleogel interface.

The EC oleogel production process, unfortunately, promotes the formation of primary oxidation products which most likely results in the formation of undesired flavors during cooking and storage. Indeed, sensory evaluations on frankfurters containing EC oleogels performed by Barbut et al. showed that panelists perceived oleogel frankfurters as "chemical" and "rancid."[170] Moreover, juiciness decreased drastically with increasing oleogel content while oiliness increased. The reduction in juiciness was as high as 50% at the lowest substitution level of 20%. The authors further stated that the addition of an antioxidant (BHA) or rosemary extracts enhanced panelists' perception which on the other hand would result in higher production costs. However, problems relating to oil deterioration might occur to a much lesser extend once raw materials are handled professionally in an industrial context.

In contrast to parboiled sausages which contain about 25 wt% fat, the fat content in liver pâtés is within the range of 28 (cased pâté) up to 50 wt% (spreadable pâté). Here, the function of the fat is to ensure a smooth texture of the pâté. Moreover, pork meat and fat are precooked before being chopped with the liver. Consequently, only liver proteins are available for stabilization of the fat globules and network formation. To promote protein adsorption, the chopping process is carried out at elevated temperatures (50–55 °C). Oleogels with either 12 or 14 wt% EC and 1.5 or 3.0 wt% glycerol monostearate (GMS) in canola oil were used to reduce the SAFA content of a liver pâté formulation by 60%.[178] Additionally, two pâtés were produced with pure pork fat and canola oil, respectively. The authors showed that hardness of pâtés at room temperature could be mimicked using either 14% EC oleogel or a mixture of 12% EC + 3% GMS. Interestingly, the sample with canola oil was only marginally softer than the pork fat control. Moreover, the sensory score hardness, oiliness, juiciness, and cohesiveness of the canola oil pâté obtained by a trained panel was almost identical with the control.[178] In contrast, the EC oleogel based product had a lower score in cohesiveness and was perceived harder while the addition of emulsifier decreased juiciness and oiliness. Not surprisingly, in off-flavor evaluation canola oil and canola oil-based oleogel (14% EC +1.5% GMS) had a score lower than the pork fat sample. This indicates that in high-fat liver pâtés the use of canola-based oleogel offers no benefit over utilizing natural canola oil.

10.3. Margarine and Spreads for Direct Consumption

In margarine and spreads, the solid fat phase is crucial to stabilize the emulsion and entrap the liquid oil. Moreover, the 3D fat crystal network ensures spreadability. Hardstock fats should hence deliver solids at ambient temperature but practically be dissolved at body temperature to avoid a waxy mouthfeel. Additionally, the disintegration of the fat crystal network coincides with the droplet stabilization failure resulting in phase inversion and hence release of flavors from the aqueous phase. Due to this, it is quite challenging to replace conventional hardstocks in margarine with oleogels. Needless to mention, a stable emulsion has to be maintained throughout the whole product life cycle. During conventional margarine production, the liquid emulsion is subjected to intense shear forces and rapid cooling rates in a series of scraped surface heat exchanger units (SSHE). Oleogels whose networks are not based on crystalline structures—like EC or sterol/sterol-ester—offer the possibility to simplify the margarine production process, since the SSHE unit becomes obsolete. Instead, liquid emulsions might be filled into containers after emulsification, provided that the desired droplet size of the aqueous phase (3–10 μm) can be stabilized throughout the process of structural development and storage.

Pickering-type emulsions were successfully produced without the addition of emulsifiers by mixing a hot oil phase containing β-sitosterol and γ-oryzanol (16 or 32 wt% on fat) and a preheated water phase (10%, 30%, 60%) under high shear conditions.[91] After emulsification, a thick liquid is obtained which solidifies during cooling and storage. The tubular structure formed by the sterol/sterol-ester system is partly lost in the presence of water due to the formation of sitosterol monohydrate crystals, as described above. This effect diminishes at higher structurant concentrations and reduced water activity (<0.9).[92] Not surprisingly, the mitigation of the sitosterol hydrate crystallization leads to a considerable increase in emulsion firmness.[92] Nevertheless, the formation of monohydrate crystals does not result in a complete breakdown of the emulsion since the rod-like hydrate crystals also contribute to the stabilization of water droplets as well. Yet, light microscopy revealed significant coarsening of water droplets within 1 week of storage which indicates that sitosterol monohydrates are less effective in preventing coalescence and thus are not suitable for margarine production.[91] Finally, the sterols and sterol-esters are significantly more expensive than conventional solid fats (Table 2), which will eventually limit their application to niche food products or pharmaceutical products since they are also known to lower lipase reaction speed and thus offer the possibility for controlled nutrient release.[90]

Plant-based waxes, on the other hand, offer the possibility to replace high-SAFA fats (hardstocks) on a larger scale as discussed in Section 4. Winkler-Moser et al. added SFX, CLX, RBX, and

BWX instead of hydrogenated or tropical oils to peanut butter to prevent oil separation.[181] The addition of waxes—especially SFX—increased oil binding capacity and reduced oil separation similar to the conventional stabilizer and samples were stable for 6 months. However, wax concentrations >0.5% produced significantly harder peanut butter. Moreover, the amount of stabilizer in peanut butter is low (typically 0.5–3%) and thus the achievable nutritional benefit is marginal.

Hwang et al. used CLX, SFX, and RBX oleogels to structure soybean oil and consequently manufacture margarine-containing lecithin, mono- and diglycerides, and skimmed milk proteins as emulsifiers.[179] After emulsification at 75 °C, the samples were left to gel in an ice bath without any additional mechanical agitation. Commercial margarine and spread samples were subjected to the same treatment prior to analysis. Interestingly, CWX samples showed phase separation directly after emulsification, which might be the result of interactions formed between the fat-soluble emulsifiers and the components of CLX. CLX typically contains approximately 80% of n-alkanes ($C_{27,29,31,33}$),[48,200] while SFX and RBX practically exclusively consist of wax esters. The difference in molecular composition could affect the success of emulsion stabilization either by reduced amounts of solid material present, or specific habit (size and shape) of the crystals, or less affinity of the solids with the interface. The latter either driven by the crystals themselves or the interaction with the emulsifiers present.

A similar effect—the failure of gel functionality due to interaction with the food matrix—has been reported for 12-HSA. Here, the fibrous crystalline structure of 12-HSA was entirely lost in the presence of lecithin due to the formation of complexes.[201] In contrast to CLX, stable and firm margarine-like emulsion could be obtained using SFX. Their firmness can be manipulated by the amount of SFX used and was found to mimic that of commercial spreads at low wax concentrations (1–2% SFX) and margarine at higher wax concentrations. Unfortunately, drop melting points determined were significantly above body temperature in formulations using more than 1 wt% wax, which indicates a rather dissatisfying sensory sensation of wax-based margarine.[179] This interpretation is further endorsed by the high disintegration temperatures obtained from DSC measurements (52–64 °C). For all samples, the values determined by pulse NMR, an analogue to SFC, was insensitive to temperature from 15–35 °C. This indicates that even though the basic structure of spreads can be reproduced, the disintegration characteristics of wax- and hardstock-based products still differ dramatically.

The same group found that SFX margarine could be produced using different plant oils.[180] They found no clear correlation of FA profile and polar components (TPC) on oleogel and margarine properties such as hardness and phase transition temperatures. However, the results indicate that oils with higher TPC tend to result in harder oleogels, while the effect was inverted in margarine samples. Since the composition of minor components is unique in each oil, the contributions of different groups of molecules to the network strength is hard to disentangle. Nevertheless, they can act as crystal habit modifiers and thus change firmness and network appearance.[209]

Unfortunately, both studies do not provide information about long-term storage of margarine samples or sensory evaluations. Thus, it remains unclear whether emulsion stability is ensured over shelf-life and if other instability effects such as coarsening of wax crystals occur. Nevertheless, mixing of low- and high-melting waxes and the use of different emulsifiers and production techniques open almost infinite possibilities to tailor wax oleogel emulsions.

10.4. Shortening/Margarine for Pastries

In contrast to bread production, the development of a gluten network is not desired in shortcrust pastries. High quantities of fat enable the coating of individual starch grains and thus prevent the extension of the gluten structure between grains. Consequently, the fat needs to be mixed into the flour easily during dough development. Furthermore, in the final product (e.g., cookies), it has to provide a sufficient amount of solid structure to ensure the typical stiffness and snap.[202] Conventionally, shortenings with no water and a defined ratio of solid fat to liquid oil are used for shortcrust pastries. Excessive amounts of water would result in immoderate gelatinization of starch and thus loss of the rigid structure. In cake dough, on the other hand, air bubbles as well as water, which make the dough rise throughout baking, need to be entrapped in the dough during the mixing process. Therefore, common cake shortenings often contain emulsifiers such as mono- and diglycerides. They will not only increase the amount of air incorporated during the mixing but also provide a more tender structure to the baked product. Consequently, oleogels which ought to replace shortenings/margarine for pastries have to comply with a wide range of requirements:

- show good mixing behavior with all ingredients
- no deoiling during mixing, baking, storage
- be able to coat starch grains to prevent extended gluten network formation
- stabilize the partly gelatinized starch in the final product
- stabilize air bubbles and water in the dough (emulsifiers needed)

Yılmaz and Öğütcü replaced conventional baking shortening (≈20% water) with sunflower- and beeswax oleogels (hazelnut oil) to produce cookies.[67] Besides testing of basic quality parameters such as hardness, moisture content, dimensions, and weight, they conducted sensory evaluations of cookies with 12 trained panelists as well as a consumer test with 200 volunteers. Moreover, they monitored hardness, moisture, and POV every 10 days over 30 days of storage. Interestingly, wax oleogel cookies were perceived harder by the trained panel, although they were objectively softer when measured, 31.8 and 36.9 N compared to 47.1 N. The reduced hardness might be due to the lower amount of water present in oleogel cookies which results in less starch gelatinization. It was mentioned before that the water content plays a crucial role for dough development, baking, and thus final cookie properties. Therefore, the same amount of water should be used for all recipes to obtain comparable results. Moreover, emulsifiers used in shortening (lecithin, mono-, and diglycerides) should be incorporated in the same quantity into oleogel formulations. However, all other ratings of the texture/flavor profile analysis with the trained panelists were equal or higher for oleogel cookies. In line with that, the consumers also preferred

the oleogel over the conventional cookies in every aspect (smell, flavor, acceptability, appearance, and texture). During storage, the hardness of the conventional cookie first increases, then decreases to and reaches its initial value after 30 days. The moisture content followed the same trend which implies retrogradation of gelatinized starch and thus syneresis followed by dehydration of the cookies. In contrast, beeswax and sunflower wax cookies showed a gradual increase in moisture content during storage. Interestingly, the hardness of SFX cookies decreased while it was the opposite in BWX samples. Since there was only little water in the oleogel cookies, this effect might be attributed to a reduced gluten network formation in SFX cookie dough due to the different composition of the waxes and firmness of the oleogels (SFX firmer). A similar effect was reported by other authors who used oleogels with different wax contents and observed that cookies softened at higher wax concentrations.[183,184,186] However, in these studies, water was added to cookie doughs and thus gelatinization occurred during baking, which contributes to the network structure as discussed at the beginning of the section. Interestingly, only one group utilized conventional shortening with pure oil.[183] Due to the lower dough viscosity, cookies prepared with pure sunflower oil had a greater width, were thinner, and twice as hard as the samples made from shortening. This indicates that the dough network entrapped less air and intensified starch gelatinization in the presence of liquid oil.

However, the results have shown that highly acceptable cookies can be produced with wax oleogels. Moreover, their properties can be modified by the wax type and concentration whereas it is surprising that a harder gel results in softer cookies. Since the water content and emulsifiers present have a pronounced impact on dough formation, air entrapment, and final cookie properties, their amount should be similar in all samples to obtain comparable results. Unfortunately, most studies do not consider emulsifiers or water within the shortening.

Wax oleogels have also been used to substitute baking shortening in gluten-free cake recently.[185] In contrast to cookie dough, more water is added to promote gelatinization of starch during baking and aid pore formation. Intense input of mechanical energy during mixing leads to the incorporation of many finely distributed air bubbles which should remain stable during the production process. Emulsifiers and fat crystals in conventional shortenings stabilize the air interface during mixing and retain moisture after baking.[202,203] Demirkesen and Mert[185] used oleogels with 10% beeswax to fully and partially replace shortenings in cakes. They found a decrease in dough overrun after mixing with increasing oleogel content. The pore size before baking was slightly smaller in oleogel samples, while it was the opposite after baking. This indicates that air bubbles were not sufficiently stabilized when wax oleogels were used. Moreover, there were significantly fewer pores than in conventional formulations which results in a decrease in dough volume after mixing.

Initial crumb and crust hardness increased with oleogel content and increased further during 7 days of storage. This indicates enhanced starch gelatinization after baking and water loss during storage. Unfortunately, the authors neither provide information about moisture content nor did they perform sensory evaluations. However, the addition of emulsifiers to wax oleogels might improve dough properties and final cake structure. Additionally, the combination of pure oils and emulsifiers should also be tested against a solid fat-containing shortening before claiming the necessity to use oleogels to structure cake doughs.

10.5. Dairy Products

Ice cream is a complex multiphase system which consists of a partially solidified aerated oil in water emulsion. The continuous phase is highly viscous and once frozen a concentrated solution of sugars, proteins, and hydrocolloids. Moreover, besides ice crystals, it contains finely dispersed semi-solid fat droplets which should form agglomerates and support the stabilization of the air/water interface. This process is aided by the addition of emulsifiers such as mono- and diglycerides. The accurate distribution and stabilization of fat droplets by proteins is needed to avoid creaming and is realized via homogenization at elevated temperatures (75 °C). Subsequently, the emulsion is allowed to ripen at 4 °C (4 h) whereas the fat solidifies inside the globules which organize to form flocs and possibly a network. Before freezing, the emulsion is commonly whipped to introduce air bubbles (10–150 μm). Higher air incorporation results in softer but less creamy ice creams. The increase in volume is usually expressed as overrun, which describes the excess volume of the final product relative to the initial emulsion volume. Commonly, SSHEs operating at low temperatures (−5 °C) are used to introduce more air into the whipped emulsion while simultaneously initiating water crystallization generating ice crystals (10–150 μm).

Moriano and Alamprese substituted milk fat (4% and 8%) in ice creams with pure sunflower oil or oleogels made of 8 and 12 wt% sitosterol/oryzanol in sunflower oil.[190] Oleogel-based ice creams with 12 wt% structurants had the highest overrun of all samples while sunflower oil-based products had the lowest (42.2% and 27.5%). Presumably, emulsifiers rather adsorb at the oil–water interface when sunflower oil is used and thus air bubble stabilization is not sufficient. In contrast, fewer emulsifiers might be needed to stabilize oleogel droplets since they solidify rather quickly upon cooling at sterol concentrations >10 wt%, and thus more emulsifier is available to stabilize the air interface. However, sitosterol can form monohydrate crystals and thus it is crucial to reduce the water activity in the continuous phase below 0.9.[92] It has been reported that milk proteins also successfully prevented monohydrate formation in model systems because they adsorb at the oleogel–water interface. Moreover, low-esterified pectin might be used to immobilize water and consequently suppress monohydrate formation.[189]

Although the utilization of sunflower oil and oleogel retarded the beginning of ice cream melting, the subsequent melting rates were much higher than in milk fat ice creams.[190] This can be attributed to the entrapment of ice crystals within the solid TAG network which retards their melting. Additionally, smaller crystals and air bubbles, as well as a more uniform distribution, is preferable since that does not only increase creaminess but also decreases the melting rate. Unfortunately, no data regarding these parameters is provided in this study. Besides, it is unclear whether sitosterol/oryzanol droplets aggregate and form a network able to stabilize air bubbles. Nevertheless, stable premixes and ice creams could be produced with sitosterol/oryzanol

oleogels, but more data is needed to understand stabilization mechanisms, storage stability, and organoleptic properties.

Wax oleogels, on the other hand, might offer the possibility to stabilize interfaces in ice cream due to their crystalline structure. It has been shown that waxes can adsorb at the interface of an w/o-emulsion if a surfactant (sorbitan monooleate) is present.[204] The authors suggested a synergistic effect of emulsifier and wax crystals which improved the interfacial rheology and did not depend on crystal shape (needle or round). Zulim Botega et al. used 10% RBX oleogels to produce ice cream with a total fat content of 10%.[191] Besides sugar and skim milk powder, the effect of a mixture of 80% saturated mono- and diglycerides and 20% polysorbate 80 at concentrations between 0.0% and 0.2% on emulsion stability, overrun, and melting was studied. Conventional milk fat and high oleic sunflower oil (HOSO) with 0.2% emulsifiers were studied as references.

The addition of RBX improved the overrun (50.8%) in comparison to HOSO (32.0%) but falls short when compared to milk fat (73.1%). Interestingly, a maximum in overrun (58.3%) was found at 0.05% emulsifier concentration. Moreover, oleogel globule size increased significantly from 1.4 μm at 0% emulsifiers to 11.3 μm at 0.2% addition. The authors found that in the presence of the small surface-active molecules, proteins were replaced at the interface and formed a shell around the oleogel droplets.[191] This process could have led to coalescence and thus larger fat globules. Nevertheless, the emulsifiers aided aggregation of fat globules at the air–cell interface. At high concentrations, the shape of air cells was distorted which might have caused destabilization and disappearance of air bubbles and thus lower overrun. Furthermore, the use of RBX oleogel nearly doubled the size of air cells compared to the milk fat sample. This is manifested in the melting speed of the ice cream samples. Although the addition of the emulsifier retarded the melting after 90 min at room temperature, 70% of both HOSO and oleogel-based ice creams were molten while the milk fat-based reference maintained 80% of its mass.

The studies conducted reveal that wax-based oleogels can deliver the same structural elements as milk fat. This means, in particular, the accumulation of partially aggregated fat globules stabilizing the air bubbles. Even though the functionality of oleogels was superior to liquid oils, the disintegration behavior is still gravely different from the reference. Nevertheless, more data is needed to tune formulations and explore processing options to create acceptable oleogel-based ice creams, for example, if the addition of selected emulsifiers improves the efficacy of air cell stabilization. Unfortunately, none of the studies considered provides information on organoleptic properties or storage stability of ice creams.

In contrast to ice creams, yoghurt is considered a gel where the aqueous phase is entrapped within a protein network. The textural properties of yoghurt such as richness are i.a. linked to its fat content and fat globule distribution. Therefore, before inoculation with lactic acid bacteria, the milk is homogenized at elevated temperatures (≈70–75 °C) to obtain fat droplets with diameters around 2 μm.[205] These should remain stable throughout the fermentation process. When the isoelectric point of caseins is reached (pH = 4.6) during acidification, they coagulate and form a 3D network in which the fat droplets are restrained as a result of interactions with domains of hydrophilic proteins.[206]

The addition of phytosterols to yoghurt, among others, resulted in a greater reduction of LDL than in other food products.[207] Consequently, the replacement of milk fat in yoghurt by phytosterol oleogels is beneficial on several levels. Moschakis et al. emulsified a 20% solution of oryzanol and a sterol-mixture in sunflower oil into an aqueous phase with polysorbate 20.[192] They used various ratios of the oryzanol:sterol-mixture (0:100; 20:80...100:0) and several phytosterol concentrations (0, 10, 20, 25...35 wt% on oil). Oleogel emulsions based on the generally recommended equimolar sterol mixture (60:40) remained stable during 60 days of storage. This is curious since it has been reported in numerous studies that the fibrillar oleogel network (see Section 5) is decomposed in the presence of water due to the formation of monohydrate crystals.[87,90–92,208]

However, emulsions with a total sterol concentration of 20% or 35% and oryzanol:sterol-mixture ratios of 0:100, 20:80, and 60:40 were dispersed in skimmed milk and subsequently fermented to obtain yoghurts with 2% or 4% lipid content. All formulations showed the characteristic gelation and acidification kinetic of a yoghurt fermentation. Yoghurts which contained 100% or 80% oryzanol showed G′ values similar to the reference. This might be due to the existence of a supportive crystalline network of hydrated crystals in the continuous phase which is visible in optical micrographs.[192] The yoghurt with an equimolar ratio (60:40) of phytosterols in the lipid phase had the lowest G′ which is likely the result of the loss of the nano fibrillar structure due to the crystallization into hydrated crystals. In contrast to the samples containing 100% or 80% oryzanol, a supportive crystal network could not be formed since the concentration and thus supersaturation of the individual phytosterol is lower in the 60:40 mixture. The results raise the question of the actual state of fat droplets (gelled or a shell of hydrated crystals) in the yoghurt. Unfortunately, the authors neither provide information about that nor did they perform sensory evaluations and storage tests of yoghurts. However, the results indicate that a gelled oil phase might not be necessary to obtain yoghurts with rheological properties similar to the milk-fat based reference. Similar results were recently obtained at the Department of Food Process Engineering at the Technical University of Berlin. Here, stable yoghurt (10 wt% fat content, 14 days' storage at 5 °C) with satisfying rheological characteristics was produced by utilizing pure, unstructured edible oils.[211]

In cream cheese, fat droplets are typically incorporated into a milk protein network similar to yoghurt. However, the fat has a greater significance with regard to organoleptic properties since cream cheese has a higher dry mass content. Full-fat products usually contain 20–26% fat, which contributes greatly to richness, spreadability, and disintegration characteristics in the mouth. Bemer et al. replaced milk fat in cream cheese with ethylcellulose and RBX-based oleogels or high oleic sunflower oil (HOSO) and compared the resulting products to commercially available cream cheese products (full-fat and zero-fat).[194] While the HOSO sample was significantly harder due to the smaller fat droplet size, RBX and EC oleogels were found to mimic firmness, spreadability, and stickiness of the full-fat cream cheese adequately. It has to be noted that the oleogel-based cream cheese samples had a different composition than the reference since they featured less moisture and total fat content but more non-fat solids than the full-fat control. Confocal laser scanning microscopy was used to

visualize the protein network and fat globules. In EC oleogel-based cream cheese, these characteristics matched the reference well, while RBX oleogel samples showed a somewhat denser protein network. The authors also performed a five-point Just About Right (JAR) test with 20 panelists, in which EC oleogel cream cheese samples were not considered. The test revealed a high acceptance level of RBX oleogel-based cream cheese in the categories of hardness, spreadability, mouthfeel, and sweetness. However, flavor and bitterness were perceived considerably worse than for the reference. This most likely applies to EC cream cheese as well, since a rancid taste was also reported when the oleogel was used in other food products.[170]

In a consecutive study which was conducted by the same group, it was found that γ- and δ- tocopherol from high oleic soybean oil were reduced in RBX cream cheese samples due to the input of thermal energy during oleogel production.[193] Malondialdehyde (MDA) and POV were higher in oleogels and increased during storage. However, these oxidation indicators were not determined in cream cheese samples and their absolute values in oleogel samples were still very low (POV < 1 mEq kg^{-1}, MDA <1.5 nmol g^{-1}). Interestingly, volatile compounds in oleogel-based cream cheese products decreased slightly during storage and were higher in the ungelled control sample. This indicates that the restriction of fat globules within the protein network could prevent the formation of oxidation products.

In summary, it can be established that oleogel applications are in most cases promising. In fat continuous products, stabilization of interfaces and distribution within the matrix is essential. In water continuous products, the fat often acts as an intermediary. Certainly, the functionality and state of the fat during and after processing need to be considered carefully. However, the broad range of structurants available at the moment enables for the selection of the most suitable system. Nevertheless, interactions with complex food matrices are often problematic so that—in the worst case—the gel falls apart as it was reported for the sterol/sterol ester system.

11. Conclusion and Perspective

The ban on trans fatty acids, the health benefits associated with a diet involving mono- and polyunsaturated fatty acids, and the negative public image of palm oil have led to a considerable push to replace or substitute conventional solid fats by healthier alternatives. Mono- and polyunsaturated fatty acids which support the health of our cardiovascular system can in their native state not provide the structure necessary for many food product applications. Oleogels, on the other hand, offer the possibility to improve the nutritional profile of foods, in particular their lipid phases, by immobilizing liquid oil rich in unsaturated FA in a non-TAG 3D network.

Various researchers made tremendous efforts to discover new oleogel systems and understand their formation and properties in the past decades. Yet, until today oleogels are not part of our daily diet. Hence, the question arises whether we lost track of our goal to provide healthier products to the consumer or if we just should cut the expectation to find the ideal oleogel system. One could argue that the price per tonne of structured oil exceeds that of, for example, palm oil by far which will be reflected in end-user pricing (Table 3). Nevertheless, prices of some structurants such as waxes will likely decline once production on a larger scale is initiated. SCX and RBX as well as ethylcellulose production, for example, have by far not exploited its full potential as was pointed in this review. Nevertheless, the price difference is mostly caused by the mark up of seed oils compared to palm oil. The broader implementation of oleogels is currently not only hampered by economical hurdles. While the situation concerning increased consumption of the structurants currently appears uncritical, the legal situation remains a bit blurred and difficult (novel food regulation) and should become clearer once products are introduced into the market.

However, the ongoing demand for healthier alternatives to SAFAs and the controversial public perception of palm oil should be sufficient to stimulate the utilization of oleogels on a bigger scale. Still, many studies dealing with applications of oleogels lack on one hand challenges under real process conditions, sensory evaluations, storage tests. On the other hand, it is not always assessed if the systems studied offer any benefit over the utilization of liquid oil. Additionally, studies based on known structurants in, for example, alternative ratios or combinations with similar continuous phases than those utilized in previous studies should preferentially only be executed when they aim at specific new insights. This is not meant to discredit these systems but rather to drive research toward studies that generate new information and help oleogels to flourish.

To this end, oleogels need to be functional, available, and affordable to a certain extent. Progress toward successful product applications can thus only be realized if the initial approaches provided by scientists are reasonable. Moreover, intricate processes which will most likely never be available on a bigger scale do not offer convenient solutions. So far, the connection between oleogel science and application in the industry is amendable. To create better understanding, scientists investigating food product applications should always contemplate: 1) the functionality of the fat, 2) its physical state during processing and 3) in the final product. Consequently, suitable structuring systems satisfying the identified critical characteristics may be chosen. Moreover, the idea to mimic all the unique properties that specific solid TAG networks provide should be abandoned to make room for new developments. This may be realized by either generating new product characteristics or yielding products similar to consumer expectations which are technologically different.

Acknowledgements

Open access funding enabled and organized by Projekt DEAL.

Data Availability Statement

Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

edible oleogel, oleogel, organogel, saturated fat alternatives, structured oils

Received: July 6, 2020
Revised: August 25, 2020
Published online:

[1] W. Kloek, Ph.D. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands, **1998**.
[2] A. Bot, E. Flöter, in *Edible Oil Processing* (Eds: G. Calliauw, R. J. Hamilton, W. Hamm), Wiley-Blackwell, Chichester, UK **2013**, pp. 223–249.
[3] J. A. Nettleton, I. A. Brouwer, J. M. Geleijnse, G. Hornstra, *Ann. Nutr. Metab.* **2017**, *70*, 26.
[4] R. P. Mensink, P. L. Zock, A. D. M. Kester, M. B. Katan, *Am. J. Clin. Nutr.* **2003**, *77*, 1146.
[5] World Health Organization, Guidelines: Saturated Fatty Acid and Trans-Fatty Acid Intake for Adults and Children (draft issued for public consultation in May 2018), WHO, Geneva **2018**.
[6] Y. Papanikolaou, J. Brooks, C. Reider, V. L. Fulgoni, *Nutr. J.* **2014**, *13*, 31.
[7] Z. Zhang, V. L. Fulgoni, P. M. Kris-Etherton, S. H. Mitmesser, *Nutrients* 416, **2018**, *10*.
[8] D. Mozaffarian, R. Clarke, *Eur. J. Clin. Nutr.* **2009**, *63*, S22.
[9] R. J. de Souza, A. Mente, A. Maroleanu, A. I. Cozma, V. Ha, T. Kishibe, E. Uleryk, P. Budylowski, H. Schünemann, J. Beyene, S. S. Anand, *BMJ* **2015**, *351*, h3978.
[10] Bundesinstitut für Risikobewertung, Höhe der derzeitigen trans-Fettsäureaufnahme in Deutschland ist gesundheitlich unbedenklich 2013.
[11] R. Micha, S. Khatibzadeh, P. Shi, S. Fahimi, S. Lim, K. G. Andrews, R. E. Engell, J. Powles, M. Ezzati, D. Mozaffarian, Global Burden of Diseases Nutrition and Chronic Diseases Expert Group NutriCoDE, *BMJ* **2014**, *348*, g2272.
[12] World Health Organization, *Replace Trans Fat* **2018**, https://apps.who.int/iris/handle/10665/331304. (accessed: June 2020).
[13] Food and Agriculture Organization of the United Nations, *STAT Crop Production Worldwide*, http://www.fao.org/faostat/en/#data/QC
[14] H. K. Gibbs, A. S. Ruesch, F. Achard, M. K. Clayton, P. Holmgren, N. Ramankutty, J. A. Foley, *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 16732.
[15] T. Guillaume, M. M. Kotowska, D. Hertel, A. Knohl, V. Krashevska, K. Murtilaksono, S. Scheu, Y. Kuzyakov, *Nat. Commun.* **2018**, *9*, 2388.
[16] P. C. West, H. K. Gibbs, C. Monfreda, J. Wagner, C. C. Barford, S. R. Carpenter, J. A. Foley, *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 19645.
[17] Thomson Reuters, Brazil farmers poised to plant record soy area in 2018–19: poll. https://www.reuters.com/article/us-brazil-grains-soybeans-idUSKCN1L61X5 (accessed: June 2020).
[18] *The World of Organic Agriculture: Statistics and Emerging Trends 2019* (Eds: H. Willer, J. Lernoud), Research Institute of Organic Agriculture FiBL and IFOAM Organics International, Frick and Bonn, Germany **2019**.
[19] G. Thompson, *HortTechnology* **2000**, *10*, 663.
[20] M. B. Katan, S. M. Grundy, P. Jones, M. Law, T. Miettinen, R. Paoletti, *Mayo Clinic Proceed.* **2003**, *78*, 965.
[21] I. Demonty, R. T. Ras, H. C. M. van der Knaap, G. S. M. J. E. Duchateau, L. Meijer, P. L. Zock, J. M. Geleijnse, E. A. Trautwein, *J. Nutr.* **2009**, *139*, 271.
[22] N. Rong, L. M. Ausman, R. J. Nicolosi, *Lipids* **1997**, *32*, 303.
[23] E. D. Co, A. G. Marangoni, *J. Am. Oil Chem. Soc.* **2012**, *89*, 749.
[24] A. Bot, E. Flöter, in *Edible Oleogels: Structure and Health Implications* (Eds: A. G. Marangoni, N. Garti), AOCS Press, Urbana, IL **2011**, pp. 49–79.
[25] A. Bot, E. Flöter, in *Edible Oleogels*, Elsevier, Cambridge, MA **2018**, pp. 31–63.
[26] W. Koch, *Ind. Eng. Chem. 29*, **1937**, 687.
[27] T. Wuestenberg, *Cellulose and Cellulose Derivatives in the Food Industry: Fundamentals and Applications*, Wiley, Chichester **2014**.
[28] Food and Agriculture Organization of the United Nations, Forest products statisitcs, http://www.fao.org/forestry/statistics/80938/en/
[29] Statistisches Bundesamt, Preise und Preisindizes für gewerbliche Produkte (Erzeugerpreise): April 2019, https://www.destatis.de/GPStatistik/servlets/MCRFileNodeServlet/DEHeft_derivate_00045560/2170200191044.pdf;jsessionid=E339B405458241456C85A9B6193BBADB (accessed: May 2019).
[30] A. C. Palmisano, M. A. Barlaz, *Microbiology of Solid Waste*, CRC-Press, Boca Raton, FL **1996**.
[31] Food and Agriculture Organization of the United Nations, Global forest products 2016: Facts and figures, http://www.fao.org/3/I7034EN/i7034en.pdf (accessed: May 2020).
[32] T. Laredo, S. Barbut, A. G. Marangoni, *Soft Matter* **2011**, *7*, 2734.
[33] A. K. Zetzl, A. J. Gravelle, M. Kurylowicz, J. Dutcher, S. Barbut, A. G. Marangoni, *Food Struct.* **2014**, *2*, 27.
[34] A. J. Gravelle, S. Barbut, M. Quinton, A. G. Marangoni, *J. Food Eng.* **2014**, *143*, 114.
[35] T. Dey, D. Kim, A. G. Marangoni, in *Edible Oleogels: Structure and Health Implications* (Eds: A. G. Marangoni, N. Garti), AOCS Press, Urbana, IL **2011**, pp. 295–312.
[36] A. Lopez-Martínez, M. A. Charó-Alonso, A. G. Marangoni, J. F. Toro-Vazquez, *Food Res. Intern.* **2015**, *72*, 37.
[37] Dow Chemicals, *ETHOCEL™: Ethylcellulose Polymers Technical Handbook: Dow Celulosics*, http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_004f/0901b8038004fb7c.pdf?filepath=eth. (accessed: March 2020).
[38] A. K. Zetzl, A. G. Marangoni, S. Barbut, *Food Funct.* **2012**, *3*, 327.
[39] A. J. Gravelle, S. Barbut, A. G. Marangoni, E. oleogels, *Food Res. Int.* **2012**, *48*, 578.
[40] A. J. Gravelle, M. Davidovich-Pinhas, A. K. Zetzl, S. Barbut, A. G. Marangoni, *Carbohydr. Polym.* **2016**, *135*, 169.
[41] M. Scharfe, Y. Ahmane, J. Seilert, J. Keim, E. Flöter, *Eur. J. Lipid Sci. Technol.* **2019**, *121*, 1800487.
[42] V. Giacintucci, C. D. Di Mattia, G. Sacchetti, F. Flamminii, A. J. Gravelle, B. Baylis, J. R. Dutcher, A. G. Marangoni, P. Pittia, *Food Hydrocolloids* **2018**, *84*, 508.
[43] R. Sánchez, J. M. Franco, M. A. Delgado, C. Valencia, C. Gallegos, *Carbohydr. Polym.* **2011**, *83*, 151.
[44] L. A. Quinchia, M. A. Delgado, T. Reddyhoff, C. Gallegos, H. A. Spikes, *Tribol. Int.* **2014**, *69*, 110.
[45] A. R. Place, *Am. J. Physiol.* **1992**, *263*, R464.
[46] J. L. Hargrove, P. Greenspan, D. K. Hartle, *Exp. Biol. Med.* **2004**, *229*, 215.
[47] C. M. Cook, T. S. Larsen, L. D. Derrig, K. M. Kelly, K. S. Tande, *Lipids* **2016**, *51*, 1137.
[48] C. D. Doan, C. M. To, M. d. Vrieze, F. Lynen, S. Danthine, A. Brown, K. Dewettinck, A. R. Patel, *Food Chem.* **2017**, *214*, 717.
[49] F. M. Alvarez-Mitre, J. A. Morales-Rueda, E. Dibildox-Alvarado, M. A. Charó-Alonso, J. F. Toro-Vazquez, *Food Res. Int.* **2012**, *49*, 580.
[50] P. A. Ochoa George, J. J. C. Eras, A. S. Gutierrez, L. Hens, C. Vandecasteele, *Waste Biomass Valorization* **2010**, *1*, 407.
[51] *Sugarcane: Agricultural Production, Bioenergy and Ethanol: Agricultural Production, Bioenergy and Ethanol* (Eds: A. Borém, C. Caldas, F. Santos), Academic Press, Amsterdam **2015**.
[52] E. Krendlinger, U. Wolfmeier, H. Schmidt, F.-L. Heinrichs, G. Michalczyk, W. Payer, W. Dietsche, K. Boehlke, G. Hohner, J. Wildgruber, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley, Chichester, UK **2010**, pp. 1–63.
[53] Food and Agriculture Organization of the United Nations, Minor oil crops— individual monographs: Rice Bran, http://www.fao.org/3/x5043e/x5043e0a.htm (accessed: May 2020).
[54] F. Shahidi, A. E. Bailey, *Bailey's Industrial Oil and Fat Products*, Wiley, New York **2005**.
[55] J. S. Godber, in *Gourmet and Health-Promoting Specialty Oils* (Eds: R. A. Moreau, A. Kamal-Eldin), Elsevier, Cambridge, **2009**, pp. 377–408.

[56] W. R. Morrison, *J. Cereal Sci.* **1988**, *8*, 1.
[57] Food and Agriculture Organization of the United Nations, New food balances, http://www.fao.org/faostat/en/#data/FBS (accessed: May 2020).
[58] H.-S. Hwang, S. Kim, M. Singh, J. K. Winkler-Moser, S. X. Liu, *J. Am. Oil Chem. Soc.* **2012**, *89*, 639.
[59] L. S. K. Dassanayake, D. R. Kodali, S. Ueno, K. Sato, *J. Oleo Sci.* **2012**, *61*, 1.
[60] C. D. Doan, D. van de Walle, K. Dewettinck, A. R. Patel, *J. Am. Oil Chem. Soc.* **2015**, *92*, 801.
[61] A. I. Blake, E. D. Co, A. G. Marangoni, *J. Am. Oil Chem. Soc.* **2014**, *91*, 885.
[62] J. C. B. Rocha, J. D. Lopes, M. C. N. Mascarenhas, D. B. Arellano, L. M. R. Guerreiro, R. L. da Cunha, *Food Res. Int.* **2013**, *50*, 318.
[63] L. S. K. Dassanayake, D. R. Kodali, S. Ueno, K. Sato, *J. Am. Oil Chem. Soc.* **2009**, *86*, 1163.
[64] Tridge, Beeswax, https://www.tridge.com/intelligences/beeswax (accessed: January 28, 2020).
[65] Peter Bengtsen, Carnauba wax background paper, https://www.scribd.com/document/221840072/Carnauba-Wax-Background-Paper (accessed: December 18, 2019).
[66] C. D. Doan, A. R. Patel, I. Tavernier, N. d. Clercq, K. van Raemdonck, D. van de Walle, C. Delbaere, K. Dewettinck, *Eur. J. Lipid Sci. Technol.* **2016**, *118*, 1903.
[67] E. Yılmaz, M. Öğütcü, *Food Funct.* **2015**, *6*, 1194.
[68] S. Martini, M. A. An, *J. Am. Oil Chem. Soc.* **2000**, *77*, 1087.
[69] U. S. Pal, R. K. Patra, N. R. Sahoo, C. K. Bakhara, M. K. Panda, *J. Food Sci. Technol.* **2015**, *52*, 4613.
[70] E. J. Rogers, S. M. Rice, R. J. Nicolosi, D. R. Carpenter, C. A. McClelland, L. J. Romanczyk, *J. Am. Oil Chem. Soc.* **1993**, *70*, 301.
[71] Z. Xu, J. S. Godber, *J. Am. Oil Chem. Soc.* **2001**, *78*, 645.
[72] S. Eslami, N. M. Esa, S. M. Marandi, G. Ghasemi, S. Eslami, *Indian J. Med. Res.* **2014**, *139*, 857.
[73] A. C. Fry, E. Bonner, D. L. Lewis, R. L. Johnson, M. H. Stone, W. J. Kraemer, *Int. J. Sport Nutr.* **1997**, *7*, 318.
[74] A. L. Gerhardt, N. B. Gallo, *J. Nutr.* **1998**, *128*, 865.
[75] G. Yoshino, T. Kazumi, M. Amano, M. Tateiwa, T. Yamasaki, S. Takashima, M. Iwai, H. Hatanaka, S. Baba, *Curr. Ther. Res. Clin. Exper.* **1989**, *45*, 543.
[76] A. G. Gopala Krishna, *Inform* **2013**, *24*, 260.
[77] M. Patel, S. N. Naik, *J. Sci. Ind. Res.* **2004**, *63*, 569.
[78] Z. Xu, J. S. Godber, *J. Am. Oil Chem. Soc.* **2000**, *77*, 547.
[79] K. Triratanasirichai, M. Singh, A. K. Anal, *Food Processing By-Products and their Utilization*, (Ed: A. K. Anal), John Wiley & Sons, Ltd, Chichester, UK **2017**, pp. 277–293. https://doi.org/10.1002/9781118432921.ch12
[80] Food and Agriculture Organization of the United Nations, Phytosterols, phytostanols and their esters: Chemical and technical assesment (CTA), http://www.fao.org/fileadmin/templates/agns/pdf/jecfa/cta/69/Phytosterols.pdf (accessed: April 2020).
[81] Food and Agriculture Organization of the United Nations, Forestry production and trade: Wood pulp chemical, global production 2018, http://www.fao.org/faostat/en/#data/FO (accessed: June 2020).
[82] P. Bajpai, *Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making*, Vol. 1, Elsevier, Amsterdam, The Netherlands **2018**.
[83] L. J. Konwar, J.-P. Mikkola, N. Bordoloi, R. Saikia, R. S. Chutia, R. Kataki, in *Waste Biorefinery: Potential and Perspectives* (Eds: A. Pandey, D.-J. Lee, S.V. Mohan, S. K. Khanal, T. Bhaskar), Elsevier, Amsterdam, The Netherlands **2018**, pp. 85–125.
[84] A. Bot, W. G. M. Agterof, *J. Am. Oil Chem. Soc.* **2006**, *83*, 513.
[85] A. Bot, R. den Adel, E. C. Roijers, C. Regkos, *Food Biophys.* **2009**, *4*, 266.
[86] A. Bot, R. den Adel, E. C. Roijers, *J. Am. Oil Chem. Soc.* **2008**, *85*, 1127.
[87] R. den Adel, P. C. M. Heussen, A. Bot, *J. Phys.: Conf. Ser.* **2010**, *247*, 12025.
[88] M. A. Rogers, A. Bot, R. S. H. Lam, T. Pedersen, T. May, *J. Phys. Chem. A* **2010**, *114*, 8278.
[89] G. Dalkas, A. B. Matheson, H. Vass, A. Gromov, G. O. Lloyd, V. Koutsos, P. S. Clegg, S. R. Euston, *Langmuir* **2018**, *34*, 8629.
[90] N. Duffy, H. C. G. Blonk, C. M. Beindorff, M. Cazade, A. Bot, S. M. J. E. Duchateau Guus, *J. Am. Oil Chem. Soc.* **2009**, *86*, 733.
[91] A. Bot, R. den Adel, C. Regkos, H. Sawalha, P. Venema, E. Flöter, *Food Hydrocolloids* **2011**, *25*, 639.
[92] H. Sawalha, R. den Adel, P. Venema, A. Bot, E. Flöter, E. van der Linden, *J. Agric. Food Chem.* **2012**, *60*, 3462.
[93] H. Sawalha, G. Margry, R. den Adel, P. Venema, A. Bot, E. Flöter, E. van der Linden, *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 295.
[94] *The MAK-Collection for Occupational Health and Safety*, Wiley-VCH, Weinheim, Germany **2002**, pp. 1–12.
[95] M. L. Wang, J. B. Morris, B. Tonnis, D. Pinnow, J. Davis, P. Raymer, G. A. Pederson, *J. Agric. Food Chem.* **2011**, *59*, 9250.
[96] L. S. Severino, D. L. Auld, M. Baldanzi, M. J. D. Cândido, G. Chen, W. Crosby, D. Tan, X. He, P. Lakshmamma, C. Lavanya, O. L. T. Machado, T. Mielke, M. Milani, T. D. Miller, J. B. Morris, S. A. Morse, A. A. Navas, D. J. Soares, V. Sofiatti, M. L. Wang, M. D. Zanotto, H. Zieler, *Agron. J.* **2012**, *104*, 853.
[97] T. Kuwahara, H. Nagase, T. Endo, H. Ueda, M. Nakagaki, *Chem. Lett.* **1996**, *25*, 435.
[98] M. A. Rogers, A. K. Smith, A. J. Wright, A. G. Marangoni, *J. Am. Oil Chem. Soc.* **2007**, *84*, 899.
[99] P. Terech, *J. Phys. II France* **1992**, *2*, 2181.
[100] S. Wu, J. Gao, T. J. Emge, M. A. Rogers, *Soft Matter* **2013**, *9*, 5942.
[101] M. A. Rogers, A. J. Wright, A. G. Marangoni, *Soft Matter* **2008**, *4*, 1483.
[102] M. A. Rogers, A. J. Wright, A. G. Marangoni, *Curr. Opin. Colloid Interface Sci.* **2009**, *14*, 33.
[103] N. E. Hughes, A. G. Marangoni, A. J. Wright, M. A. Rogers, J. W. E. Rush, *Trends Food Sci. Technol.* **2009**, *20*, 470.
[104] K. Iwanaga, T. Sumizawa, M. Miyazaki, M. Kakemi, *Int. J. Pharm.* **2010**, *388*, 123.
[105] C. L. Esposito, V. Tardif, M. Sarrazin, P. Kirilov, V. G. Roullin, *Mater. Sci. Eng., C* **2020**, *114*, 110999.
[106] A. I. Romoscanu, R. Mezzenga, *Langmuir* **2006**, *22*, 7812.
[107] R. Mezzenga, S. Ulrich, *Langmuir* **2010**, *26*, 16658.
[108] I. Tavernier, Ph.D. Thesis, Ghent, Belgium **2018**.
[109] I. Tavernier, A. R. Patel, P. van der Meeren, K. Dewettinck, *Food Hydrocolloids* **2017**, *65*, 107.
[110] A. R. Patel, P. S. Rajarethinem, N. Cludts, B. Lewille, W. H. d. Vos, A. Lesaffer, K. Dewettinck, *Langmuir* **2015**, *31*, 2065.
[111] A. de Vries, J. Hendriks, E. van der Linden, E. Scholten, *Langmuir* **2015**, *31*, 13850.
[112] A. de Vries, A. Wesseling, E. van der Linden, E. Scholten, *J. Colloid Interface Sci.* **2017**, *486*, 75.
[113] I. Tavernier, C. D. Doan, P. van der Meeren, B. Heyman, K. Dewettinck, *Eur. J. Lipid Sci. Technol.* **2018**, *120*, 1700393.
[114] A. de Vries, D. Jansen, E. van der Linden, E. Scholten, *Food Hydrocolloids* **2018**, *79*, 100.
[115] E. Scholten, A. de Vries, in *Handbook of Food Structure Development* (Eds: F. Spyropoulos, A. Lazidis, I. Norton), Royal Society of Chemistry, Cambridge **2019**, pp. 150–174.
[116] S. Plazzotta, S. Calligaris, L. Manzocco, *Food Res. Int.* **2020**, *132*, 109099.
[117] P. M. Meissner, J. K. Keppler, H. Stöckmann, K. Schwarz, *Food Chem.* **2020**, *328*, 127123.
[118] A. de Vries, Y. Lopez Gomez, B. Jansen, E. van der Linden, E. Scholten, *ACS Appl. Mater. Interfaces* **2017**, *9*, 10136.

[119] P. M. Meissner, J. K. Keppler, H. Stöckmann, K. Schrader, K. Schwarz, *Eur. J. Lipid Sci. Technol.* **2019**, *121*, 1800479.
[120] United States Department of Agriculture, Dairy Market News: Dry Whey Products 2011–2019, https://www.ams.usda.gov/market-news/dairy (accessed: June 2020).
[121] T. Affertsholt, D. Pedersen, *Ingredient Market* https://www.foodingredientsfirst.com/Twofi.html (accessed: June 2020).
[122] United States Department of Agriculture, Dairy Market News, https://www.ams.usda.gov/market-news/dairy
[123] World Health Organization, *Global Action Plan for the Prevention and Control of Noncommunicable Diseases: 2013–2020*, World Health Organization, Geneva, Switzerland **2013**.
[124] M. H. Forouzanfar, A. Afshin, L. T. Alexander, H. R. Anderson, Z. A. Bhutta, S. Biryukov, M. Brauer, R. Burnett, K. Cercy, F. J. Charlson, A. J. Cohen, L. Dandona, K. Estep, A. J. Ferrari, J. J. Frostad, N. Fullman, P. W. Gething, W. W. Godwin, M. Griswold, S. I. Hay, Y. Kinfu, H. H. Kyu, H. J. Larson, X. Liang, S. S. Lim, P. Y. Liu, A. D. Lopez, R. Lozano, L. Marczak, G. A. Mensah, et al., *Lancet* **2016**, *388*, 1659.
[125] G. Delgado-Pando, P. Celada, F. J. Sánchez-Muniz, F. Jiménez-Colmenero, B. Olmedilla-Alonso, *Eur. J. Nutr.* **2014**, *53*, 83.
[126] C. M. O'Sullivan, S. Barbut, A. G. Marangoni, *Trends Food Sci. Technol.* **2016**, *57*, 59.
[127] S. Murdan, *Expert Opin. Drug Delivery* **2005**, *2*, 489.
[128] A. Speranza, M. G. Corradini, T. G. Hartman, D. Ribnicky, A. Oren, M. A. Rogers, *J. Agric. Food Chem.* **2013**, *61*, 6505.
[129] W. Limpimwong, T. Kumrungsee, N. Kato, N. Yanaka, M. Thongngam, *J. Funct. Foods* **2017**, *39*, 250.
[130] J. Alvarez-Ramirez, E. J. Vernon-Carter, Y. Carrera-Tarela, A. Garcia, C. Roldan-Cruz, *LWT* **2020**, *130*, 109701.
[131] J. E. Norton, Y. Gonzalez Espinosa, R. L. Watson, F. Spyropoulos, I. T. Norton, *Food Funct.* **2015**, *6*, 663.
[132] D. J. McClements, E. A. Decker, Y. Park, J. Weiss, *Food Biophys.* **2008**, *3*, 219.
[133] D. J. McClements, E. A. Decker, Y. Park, *Crit. Rev. Food Sci. Nutr.* **2008**, *49*, 48.
[134] A. J. Martins, A. A. Vicente, L. M. Pastrana, M. A. Cerqueira, *Food Sci. Human Wellness* **2020**, *9*, 31.
[135] EFSA, *EFSA J.* **2012**, *10*, 2946.
[136] EFSA, *EFSA J.* **2012**, *10*, 2880.
[137] M. Younes, P. Aggett, F. Aguilar, R. Crebelli, B. Dusemund, M. Filipič, M. J. Frutos, P. Galtier, D. Gott, U. Gundert-Remy, G. G. Kuhnle, J.-C. Leblanc, I. T. Lillegaard, P. Moldeus, A. Mortensen, A. Oskarsson, I. Stankovic, I. Waalkens-Berendsen, R. A. Woutersen, M. Wright, P. Boon, D. Chrysafidis, R. Gürtler, P. Mosesso, P. Tobback, A. M. Rincon, Z. Horvath, C. Lambré, *EFSA J.* **2017**, *15*, e05045.
[138] V. Bampidis, G. Azimonti, M. d. L. Bastos, H. Christensen, B. Dusemund, M. Kos Durjava, M. Kouba, M. López-Alonso, S. López Puente, F. Marcon, B. Mayo, A. Pechová, M. Petkova, F. Ramos, Y. Sanz, R. E. Villa, R. Woutersen, G. Bories, J. Gropp, C. Nebbia, M. L. Innocenti, G. Aquilina, *EFSA J.* **2020**, *18*, e06210.
[139] EFSA, *EFSA J.* **2012**, *10*, 2659.
[140] EFSA, *EFSA J.* **2005**, *3*, 211.
[141] D. Turck, J. Castenmiller, S. d. Henauw, H. K. I. irsch-Ernst, J. Kearney, A. Maciuk, I. Mangelsdorf, H. J. McArdle, A. Naska, C. Pelaez, K. Pentieva, A. Siani, F. Thies, S. Tsabouri, M. Vinceti, F. Cubadda, T. Frenzel, M. Heinonen, R. Marchelli, M. Neuhäuser-Berthold, M. Poulsen, J. R. Schlatter, H. van Loveren, W. Gelbmann, H. K. Knutsen, *EFSA J.* **2020**, *18*, e06135.
[142] Scientific Committee on Food, Opinion of the scientific committe on food on a request for the safety assessment of the use of phytosterol esters in yellow fat spreads, https://ec.europa.eu/food/sites/food/files/safety/docs/sci-com_scf_out56_en.pdf
[143] M. E. Lowe, *J. Lipid Res.* **2002**, *43*, 2007.
[144] Y. T. Liang, W. T. Wong, L. Guan, X. Y. Tian, K. Y. Ma, Y. Huang, Z.-Y. Chen, *Atherosclerosis* **2011**, *219*, 124.
[145] K. B. Wheeler, Garleb, K. A., *Int. J. Sport Nutr.* **1991**, *1*, 170.
[146] W. H. Ling, P. J. H. Jones, *Life Sci.* **1995**, *57*, 195.
[147] E. Kobayashi, J. Ito, S. Kato, K. Sawada, M. Matsuki, H. Hashimoto, T. Miyazawa, K. Nakagawa, *Food Funct.* **2016**, *7*, 4816.
[148] C. Perez-Ternero, M. Alvarez de Sotomayor, M. D. Herrera, *J. Funct. Foods* **2017**, *32*, 58.
[149] T. A. Miettinen, T. E. Strandberg, H. Gylling, *Arterioscler., Thromb., Vasc. Biol.* **2000**, *20*, 1340.
[150] R. Ayesh, J. A. Weststrate, P. N. Drewitt, P. A. Hepburn, *Food Chem. Toxicol.* **1999**, *37*, 1127.
[151] J. A. Weststrate, R. Ayesh, C. Bauer-Plank, P. N. Drewitt, *Food Chem. Toxicol.* **1999**, *37*, 1063.
[152] Scientific Committee on Food, General view of the Scientific Committee on Food on the long-term effects of the intake of elevated levels of phytosterols from multiple dietary sources with particular attention to the effects on ß-carotene, https://ec.europa.eu/food/sites/food/files/safety/docs/sci-com_scf_out143_en.pdf
[153] R. P. Mensink, S. Ebbing, M. Lindhout, J. Plat, M. M. A. van Heugten, *Atherosclerosis* **2002**, *160*, 205.
[154] EFSA, *EFSA Journal* **2007**, *5*, 615.
[155] M. Younes, P. Aggett, F. Aguilar, R. Crebelli, A. Di Domenico, B. Dusemund, M. Filipič, M. Jose Frutos, P. Galtier, D. Gott, U. Gundert-Remy, G. Georg Kuhnle, C. Lambré, J.-C. Leblanc, I. T. Lillegaard, P. Moldeus, A. Mortensen, A. Oskarsson, I. Stankovic, P. Tobback, I. Waalkens-Berendsen, M. Wright, A. Tard, S. Tasiopoulou, R. A. Woutersen, *EFSA Journal* **2018**, *16*, e05047.
[156] T. A. Stortz, A. G. Marangoni, *Trends Food Sci. Technol.* **2011**, *22*, 201.
[157] A. Wendt, K. Abraham, C. Wernecke, J. Pfeiffer, E. Flöter, *J. Am. Oil Chem. Soc.* **2017**, *94*, 1131.
[158] T. A. Stortz, A. K. Zetzl, S. Barbut, A. Cattaruzza, A. G. Marangoni, *Lipid Technol.* **2012**, *24*, 151.
[159] T. A. Stortz, A. G. Marangoni, *Food Res. Int.* **2013**, *51*, 797.
[160] T. A. Stortz, D. C. d. Moura, T. Laredo, A. G. Marangoni, *RSC Adv.* **2014**, *4*, 55048.
[161] T. A. Stortz, T. Laredo, A. G. Marangoni, *Food Biophys.* **2015**, *10*, 253.
[162] T.-A. L. Do, J. R. Mitchell, B. Wolf, J. Vieira, *React. Funct. Polym.* **2010**, *70*, 856.
[163] S. Marty, K. Baker, E. Dibildox-Alvarado, J. N. Rodrigues, A. G. Marangoni, *Food Res. Int.* **2005**, *38*, 1189.
[164] S. Marty, K. W. Baker, A. G. Marangoni, *Food Res. Int.* **2009**, *42*, 368.
[165] E. Panagiotopoulou, T. Moschakis, E. Katsanidis, *LWT – Food Sci. Technol.* **2016**, *73*, 351.
[166] T. Moschakis, E. Panagiotopoulou, E. Katsanidis, *LWT – Food Sci. Technol.* **2016**, *73*, 153.
[167] A. J. Martins, J. M. Lorenzo, D. Franco, A. A. Vicente, R. L. Cunha, L. M. Pastrana, J. Quiñones, M. A. Cerqueira, *Eur. J. Lipid Sci. Technol.* **2019**, *121*, 1900111.
[168] D. Franco, A. J. Martins, M. López-Pedrouso, M. A. Cerqueira, L. Purriños, L. M. Pastrana, A. A. Vicente, C. Zapata, J. M. Lorenzo, *J. Sci. Food Agric.* **2020**, *100*, 218.
[169] S. Barbut, J. Wood, A. Marangoni, *Meat Sci.* **2016**, *122*, 155.
[170] S. Barbut, J. Wood, A. G. Marangoni, *J Food Sci.* **2016**, *81*, C2183.
[171] S. Barbut, A. Marangoni, *Meat Sci.* **2019**, *149*, 9.
[172] S. Barbut, J. Wood, A. Marangoni, *Meat Sci.* **2016**, *122*, 84.
[173] L. Adili, L. Roufegarinejad, M. Tabibiazar, H. Hamishehkar, A. Alizadeh, *LWT* **2020**, *126*, 109277.
[174] A. Aliasl Khiabani, M. Tabibiazar, L. Roufegarinejad, H. Hamishehkar, A. Alizadeh, *Food Chem.* **2020**, *333*, 127446.
[175] S. L. da Silva, J. T. Amaral, M. Ribeiro, E. E. Sebastião, C. Vargas, F. d. Lima Franzen, G. Schneider, J. M. Lorenzo, L. L. M. Fries, A. J. Cichoski, P. C. B. Campagnol, *Meat Sci.* **2019**, *149*, 141.

[176] J. Gómez-Estaca, A. M. Herrero, B. Herranz, M. D. Álvarez, F. Jiménez-Colmenero, S. Cofrades, *Food Hydrocolloids* **2019**, *87*, 960.
[177] A. J. Martins, J. M. Lorenzo, D. Franco, M. Pateiro, R. Domínguez, P. E. S. Munekata, L. M. Pastrana, A. A. Vicente, R. L. Cunha, M. A. Cerqueira, *Gels* **2020**, *6*, 17.
[178] S. Barbut, A. G. Marangoni, U. Thode, B. E. Tiensa, *J. Food Sci.* **2019**, *84*, 2646.
[179] H.-S. Hwang, M. Singh, E. L. Bakota, J. K. Winkler-Moser, S. Kim, S. X. Liu, *J. Am. Oil Chem. Soc.* **2013**, *90*, 1705.
[180] H.-S. Hwang, M. Singh, J. K. Winkler-Moser, E. L. Bakota, S. X. Liu, *J. Food Sci.* **2014**, *79*, C1926.
[181] J. K. Winkler-Moser, J. Anderson, J. A. Byars, M. Singh, H.-S. Hwang, *J. Am. Oil Chem. Soc.* **2019**, *96*, 1235.
[182] G. Fayaz, S. A. H. Goli, M. Kadivar, *J. Am. Oil Chem. Soc.* **2017**, *94*, 47.
[183] B. Mert, I. Demirkesen, *LWT – Food Sci. Technol.* **2016**, *68*, 477.
[184] B. Mert, I. Demirkesen, *Food Chem.* **2016**, *199*, 809.
[185] I. Demirkesen, B. Mert, *J. Am. Oil Chem. Soc.* **2019**, *96*, 545.
[186] A. Jang, W. Bae, H.-S. Hwang, H. G. Lee, S. Lee, *Food Chem.* **2015**, *187*, 525.
[187] S. Onacik-Gür, A. Żbikowska, *J. Food Sci. Technol.* **2020**, *57*, 1609.
[188] T. D. Kammegne, *Bachelor Thesis*, Technical University Berlin, Berlin **2015**.
[189] K. Lubosch, *Diplomarbeit*, Technical University Berlin, Berlin **2015**.
[190] M. E. Moriano, C. Alamprese, *LWT – Food Sci. Technol.* **2017**, *86*, 371.
[191] D. C. Zulim Botega, A. G. Marangoni, A. K. Smith, H. D. Goff, *J. Food Sci.* **2013**, *78*, C1334.
[192] T. Moschakis, I. Dergiade, A. Lazaridou, C. G. Biliaderis, E. Katsanidis, *J. Funct. Foods* **2017**, *33*, 386.
[193] C. Park, H. L. Bemer, F. Maleky, *J. Am. Oil Chem. Soc.* **2018**, *95*, 1267.
[194] H. L. Bemer, M. Limbaugh, E. D. Cramer, W. J. Harper, F. Maleky, *Food Res. Int.* **2016**, *85*, 67.
[195] T. A. Stortz, Ph.D. Thesis, University of Guelph, Canada **2014**.
[196] S. T. Beckett, *The Science of Chocolate*, Royal Society of Chemistry, Cambridge **2018**.
[197] M. K. Youssef, S. Barbut, *Meat Sci.* **2009**, *82*, 228.
[198] J. Park, K. S. Rhee, J. T. Keeton, K. C. Rhee, *J. Food Sci.* **1989**, *54*, 500.
[199] E. J. Marquez, E. M. Ahmed, R. L. West, D. D. Johnson, *J. Food Sci.* **1989**, *54*, 867.
[200] J. F. Toro-Vazquez, J. A. Morales-Rueda, E. Dibildox-Alvarado, M. Charó-Alonso, M. Alonzo-Macias, M. M. González-Chávez, *J. Am. Oil Chem. Soc.* **2007**, *84*, 989.
[201] T. Tamura, M. Ichikawa, *J. Am. Oil Chem. Soc.* **1997**, *74*, 491.
[202] I. P. Freeman, S. M. Melnikov, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley, Chichester, UK **2010**, pp. 1–24.
[203] B. S. Ghotra, S. D. Dyal, S. S. Narine, *Food Res. Int.* **2002**, *35*, 1015.
[204] Q. Ma, W. Wang, Y. Liu, J. Yang, B. Shi, J. Gong, *Colloids Surf. A* **2017**, *518*, 73.
[205] G. Corrieu, C. Béal, in *Encyclopedia of Food and Health* (Eds: B. Caballero, F. Toldrá, P. M. Finglas), Elsevier Science, Burlington, UK **2015**, pp. 617–624.
[206] R. C. Chandan, in*Yogurt in Health and Disease Prevention*, Elsevier, Oxford **2017**, pp. 31–47.
[207] S. S. Abumweis, R. Barake, P. J. H. Jones, *Food Nutr. Res.* **2008**, *52*, 1811.
[208] H. Sawalha, P. Venema, A. Bot, E. Flöter, R. d. Adel, E. van der Linden, *J. Am. Oil Chem. Soc.* **2015**, *92*, 1651.
[209] Scharfe, unpublished.
[210] KahlWax GmbH & Co. K.G., personal communication.
[211] Conty, Valentina; Scharfe, Maria, Technical University Berlin.
[212] https://www.cfsanappsexternal.fda.gov/scripts/fdcc/index.cfm?set=FoodSubstances (accessed: August 2020).
[213] https://www.cfsanappsexternal.fda.gov/scripts/fdcc/index.cfm?set=GRASNotices (accessed: August 2020).
[214] Union List Novel Food: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32017R2470 (accessed: August 2020).