Food Engineering Reviews
https://doi.org/10.1007/s12393-024-09379-1

Design of Fat Alternatives Using Saturated Monoglycerides

Sofia Melchior[1] · Stella Plazzotta[1] · Song Miao[2] · Lara Manzocco[1] · Maria Cristina Nicoli[1] · Sonia Calligaris[1]

Received: 7 December 2023 / Accepted: 16 June 2024

Abstract
Traditional fats, used in the formulation of many high-consumption foods are characterized by the presence of a fat crystal network mainly made of saturated fatty acids (SFA). Despite conferring food unique structural and sensory properties, the lipidic composition of traditional fats has raised increasing concerns associated with the spread of diet-related non-communicable diseases. Fat substitution with alternatives characterized by a more equilibrated lipid composition is thus unanimously considered a priority to increase the food nutritional profile and sustainability. In this context, the structuring of liquid oils into semi-solid materials with a composition rich in unsaturated fatty acids but structural properties analogous to that of traditional SFA-rich fats is particularly promising. To this aim, a plethora of structuring molecules has been proposed to date. Among them, saturated monoglycerides (MGs) have the peculiar ability to self-assemble into several different hierarchical structures, which can be exploited to prepare fat alternatives. Depending on system composition and environmental conditions, MG-based hydrogels, hydro-foams, oleogels, oleo-foam and structured emulsions can be obtained. This review describes the structural properties of these MG-based fat alternatives, along with the formulation and processing factors affecting MG self-assembly capacity. An approach for the design of food using these promising structures is then presented along with a discussion of their potential functionalities.

Keywords Fat replacers · Monoglycerides · Hydrogel · Oleogel

Introduction

Today obesity and overweight are major public health issues globally [1]. This situation is well recognized to increase the risk for the onset of many non-communicable diseases (NCD) (e.g., cardiovascular diseases, Type II diabetes, obesity, stroke, metabolic syndrome, and other cholesterol-associated health issues). The population is at high risk of developing NCD associated with obesity and overweight, with children, adolescents and the elderly presenting a particularly high risk [2]. Despite there are many predisposing factors, unbalanced food consumption and dietary patterns, in association with a sedentary lifestyle, are recognized as pivotal factors in promoting the onset of NCD. In particular, a wide portion of the global population is following unhealthy diets in terms of fat intake. Available scientific data and clinical evidence concur that replacing saturated fatty acids (SFA) with polyunsaturated and/or monounsaturated ones (PUFA and/or MUFA) has favorable effects on clinical endpoints related to NCD. Similarly, the complete removal of trans fatty acids (TFA) has been demonstrated to have beneficial effects on serum lipid concentration and cardiovascular disease (CVD) risk [3]. Thus, the international community highly demands strategies to obtain healthier foods by changing their lipid profile [4]. This could favor the transition to more "sustainable-healthy diets", *i.e.*, dietary patterns that promote all dimensions of individuals' health and well-being, as clearly stated in strategic documents of many global entities [5–7]. Despite these international indications, many food products still contain large amounts of animal fats, tropical oils, margarine, and shortenings, which are rich in SFA, or even TFA deriving from hydrogenation processes. Table 1 shows examples of food product categories with high SFA content. The majority of these foods are staple foods at a high frequency of consumption by all population

✉ Lara Manzocco
lara.manzocco@uniud.it

[1] Department of Agricultural, Food, Environmental and Animal Sciences University of Udine, Via Sondrio 2/A, 33100 Udine, Italy

[2] Teagasc Food Research Center, Moorepark, Fermoy, Co. Cork P61 C996, Ireland

Published online: 11 July 2024

Table 1 Product categories at high content of fat and saturated fatty acids (SFA)

Product category	Examples	Fat content range (wt%)	SFA content range (wt%)
Seasoning	Butter	81–82	45–46
	Palm oil	100	49–50
	Coconut oil	100	83–86
	Margarine	80–81	11–27
	Lard	100	39–46
Bakery products	Biscuits	14–30	8–17
	White bread	2–5	1–2
	Sweet bread	10–12	4–7
	Crackers	14–21	2–5
	Laminated products	9–39	5–12
	Cakes	9–23	1–10
Chocolate-based products	Candy chocolate	30–32	18–20
	Spreads	30–37	4–28
Dairy products	Cheese	11–34	7–20
	Ice-cream	8–11	2–7
	Whipped creams	18–36	11–20
Meat-based products	Frankfurters	9–26	1–9
	Sausages	17–29	6–11
	Hamburgers	10–11	3–4
Plant-based analogues	Frankfurters	9–14	1–2
	Sausages	7–18	1–3
	Hamburgers	14–19	5–7
	Cheese	21–29	14–17
	Spreads	45–64	7–9

Compositional data come from the USDA [8] and CREA [9] databases, and from market surveys

categories. The list also includes novel plant-based products intended as meat or dairy alternatives.

The availability of these products on the market is progressively and quickly increasing to follow the global trend of switching to a more plant-based diet [10]. The large use of these fats is associated with their outstanding functionalities, making fats multipurpose ingredients, applicable in many food formulations to modulate food structure (aeration and lightness), rheological properties (plasticity and texture), and sensory characteristics (taste, color, flavor, crispiness, and creaminess). Due to their peculiar technological and sensory functionalities, the partial or total replacement of fats in foods without impacting the final quality and acceptance of the product is still challenging. For this reason, in recent years, many research efforts have been dedicated to finding effective strategies for fat replacement to allow the shift toward healthier lipid-containing foods.

The ideal fat alternative should reduce the total fat and/or total saturated fat content while maintaining consumer acceptance, demonstrating similar technological functionalities without introducing additional health or environmental risks. Furthermore, the alternative fat should withstand the processing conditions typically suffered by fat-containing matrices during food production as well as assure the stability during storage of the food made thereof.

In this context, the possibility of structuring liquid oils deriving from plants or fish, rich in unsaturated fatty acids, into viscoelastic materials is of particular interest. To this aim, today a plethora of structuring molecules have been proposed. In general, such molecules are able to organize themselves at different lengths of scales, generating a viscoelastic material with mechanical and rheological properties comparable to those of the traditional fat. Among them, the structuring capacity of saturated monoglycerides (MGs) has raised the interest of both researchers and food producers. This is due to the ability of these molecules to self-assemble into different hierarchical structural organizations depending on system composition and environmental conditions.

The objective of this review is to provide a critical analysis of the different structural organizations of MGs, which could be exploited to develop fat alternatives. The processing and compositional factors affecting MG self-assembly capacity are also reviewed, emphasizing possible food applications.

Monoglycerides as Structuring Compounds

MGs are amphiphilic molecules consisting of one fatty acid esterified to a glycerol backbone. They are polar lipids classified based on carbon chain length and degree of saturation of the fatty acid moiety, mainly produced by direct esterification of glycerol with fatty acids or glycerolysis of fats [11]. Today, MGs find application in several food products, mainly as emulsifiers and anti-staling agents. Based on EU regulation 1333/2008 [12], MGs are allowed to be used in foods as additives (E471) with no need for a numerical acceptable daily intake (ADI), as reported in a recent re-evaluation of EFSA [13]. Similarly, they are compliant with the Generally Recognised As Safe status (GRAS) of the Food & Drug Administration in US.

Due to the peculiar self-assembly capacity in water, oil, and multiphase environments, MGs have been used as structuring molecules able to generate a wide variety of fat alternatives, embedding oil, water or both solvents.

MG-based structured materials claimed as fat alternatives should have structural properties mimicking those of traditional plastic fats. In particular, from a rheological point of view, these systems should exhibit gel-like behavior. Gels are defined as a continuous, three-dimensional network of connected molecules or particles entrapping a large volume of a continuous liquid phase [14]. Conventionally, gels are classified, based on the entrapped liquid phase, into: (i) hydrogels, when the immobilized liquid is an aqueous phase; (ii) oleogels, when an oil is the solvent; (iii) emulsion-gels, when the network is able to entrap both a water and an oil phase. In the latter case, both oil-in-water (O/W) and water-in-oil (W/O) emulsion-gels can be obtained depending on the continuous phase composition. When water-gelling compounds are added, a particular type of gelled emulsions is obtained, commonly referred to as bigels, in which both the water and oil phase are gelled [15]. If the amount of the dispersed phase is particularly high, high internal phase emulsions (HIPE) can be prepared, defined as concentrated emulsions characterized by a volume fraction of the dispersed phase above 0.70 [16, 17]. Starting from hydrogels and oleogels, foams could be also obtained by incorporating and embedding air.

Independently on the environment composition, the final gel structure is the result of the multi-level organization, from nano- to micro- up to macro-structure of MGs. Table 2 reports a schematic representation of the nano- and micro-level structural organization of the different MG-based structures.

Independently on the solvent/s involved, MGs in gelled systems are organized at the nano-level in bilayers, in which the alkyl chains are crystallized. At the nano-level, MGs could crystallize in α and β forms, leading to the formation of systems called, respectively α-gel and coagel [18, 19]. Since β crystals are the most thermodynamically stable, α-gels eventually convert into coagels over time. Based on this, MG system aging can be quantified based on the Coagel Index (CI, Eq. 1), which is the ratio between the melting enthalpy of both α-gel and coagel (ΔH_1) and that of only the α-gel (ΔH_2) [18, 20].

$$CI = \Delta H_1 / \Delta H_2 \tag{1}$$

The MG crystals further interact at the micro-level to form a network embedding the solvent/s between the MG bilayers. The strength of the MG network finally determines the macroscopic features of the system.

All the systems reported in Table 2 can be prepared by applying basically three main unit operations, namely, heating, mixing and cooling, that are commonly used and easily applicable in the food sector.

In all cases, the first step of MG-based structure preparation is heating above the melting point of the selected MGs. Upon heating, MGs form a lyotropic phase, where the MG molecules self-assemble in lamellar bilayers. When MGs self-organized in water, the hydrophobic tails are located inside of the MG bilayer (Table 2A). Contrarily, when MGs self-assemble in oil, the MGs form reverse lamellas, where the hydrophilic heads are located inside the structure (Table 2C).

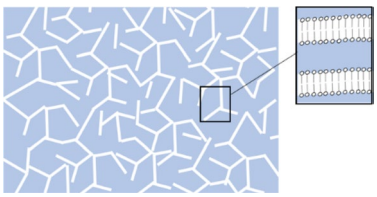
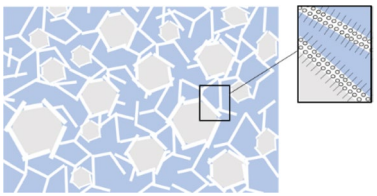
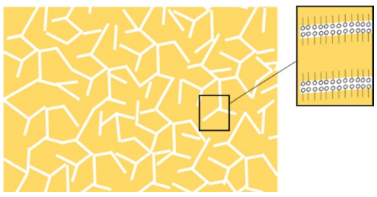
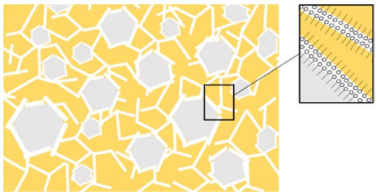
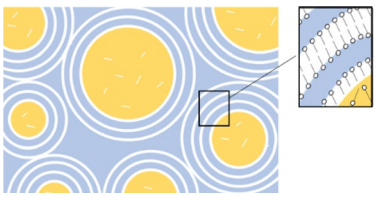
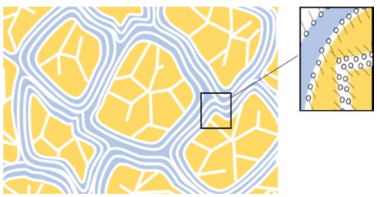
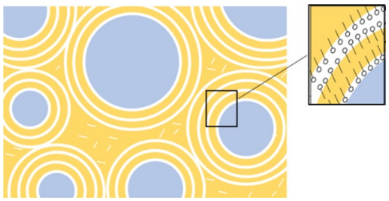
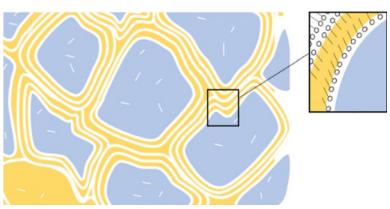
When a biphasic system (O/W and W/O emulsion-gels) is prepared (Table 2E-H), MGs interact with both the water and oil phases displacing the tails in the lipid phase and the heads in the hydrophilic environment. In this case, a mixing step is essential, to allow the dispersion of the dispersed phase in the continuous one.

Finally, a cooling step is performed to reach a temperature lower than MG crystallization point (T_c). In this way, lamellar phases transform into a crystalline structure with a polymorphic rearrangement that depends on the processing conditions. Afterward, crystallized bilayers organize into lamellar platelets that further grow leading to the formation of the three-dimensional crystalline network.

Additional processing steps can also be applied to further modulate the system structural properties. For example, during or after cooling, air can be incorporated by whipping, to prepare hydro- (Table 2B) or oleo-(Table 2D) foams [21]. In these systems, the air bubbles are stabilized according to a Pickering mechanism, due to the jamming of crystalline MG particles at the air-solvent interface [22, 23].

Moreover, drying of O/W emulsion-gels was demonstrated to lead to a HIPE system (Table 2F and H) with improved rheological properties [24].

Table 2 Schematic representation of the micro- and nano-structure of the main MG-based structures

MG-based structures	Continuous phase	Schematic representation of micro- and nano-structure
Hydrogel (A)	Water	
Hydrofoam (B)	Water	
Oleogel (C)	Oil	
Oleofoam (D)	Oil	
Oil-in-water gelled emulsion (E)	Water	
Oil-in-water high internal phase emulsion (HIPE) (F)	Water	
Water-in-oil gelled emulsion (G)	Oil	
Water-in-oil high internal phase emulsion (HIPE) (H)	Oil	

Yellow: oil phase; Blue: aqueous phase; Grey: air phase; White: MG network

Factors Affecting the MG-based Structures

Different compositional and processing factors can be modulated to steer the structural properties of MG-based structures, as reported in Fig. 1.

Compositional Factors

MG Bilayer

For all the systems, a critical role is played by the characteristics of the MGs. Saturated MGs are the best performing in the attempt to obtain fat alternatives, due to their ability to crystallize at room temperature [25]. Despite containing SFA, their structuring ability is exerted at low concentration, so that their use in the preparation of fat alternatives results in a significant reduction of SFA in the final formulation. Among saturated MGs, glycerol monopalmitate (C-16:0) and monostearate (C-18:0) are the ones more exploited in fat replacer preparation, due to their crystallization behavior [26]. Also, commercial mixtures of C-16:0 and C-18:0 MGs (40–60% and 60–40%) were successfully applied to prepare fat replacers, with particular reference to hydrogels and O/W emulsions [22, 27–30]. Such commercial mixtures present a range of melting and crystallization temperatures and a more stable polymorphic behavior than pure MG components [26]. Lower chain lengths generally lead to impaired structural features of the final system, due to the lower melting temperature of short- and medium-chain MG [11]. Recently, attention has been paid in the literature on the structuring ability of MGs containing unsaturated fatty acids (e.g., oleic, linoleic, and linolenic acids), to maximize the health benefits deriving from the substitution of SFA-rich fats with fat replacers containing gelators based on PUFA and MUFA [31].

The knowledge of these molecular characteristics of MGs is pivotal to predicting the self-assembly structure that can be obtained. In this regard, the dimensionless packing parameter (p, Eq. 2) considers the MG molecular volume (v) and length (l), and the cross-sectional area of the polar head group (a) [32].

$$p = v/al \tag{2}$$

For $p = 1$ vesicles with a flat bilayer are formed; for $p < 1$, O/W self-assembly structures such as micelles are formed; for $p > 1$, reversal W/O micelles can be obtained.

MG concentration should be also carefully optimized. Even if in the case of hydrogels and oleogels, 2–3 wt% content of MGs has been suggested as able to gel water and oils, a minimum amount of 5 wt% is usually required to generate a material mimicking fats [27, 28, 33]. In fact, the increase in MG concentration results in structure strengthening, due to higher presence of reactive groups available for networking [34–36]. Hydrofoams and oleofoams can be formed even at MG concentrations as low as 3 wt%, since structuring effect derives not only from the MG content but also from the presence of water-air or oil-air interfaces [37]. In these systems, above a threshold MG concentration, foaming is not possible, due to the excessive firmness of the initial hydrogel or oleogel, hindering air incorporation [38]. Moving to emulsion gels, Batte et al. [39, 40] and Marangoni et al. [41] demonstrated that water/MG ratio is the key compositional factor affecting the gelled emulsion properties. In particular, the water content and MG:water ratio cannot be lower than 25% and 1:5 w/w, respectively, to allow for a proper MG bilayer hydration and sufficient oil encapsulation [42].

The MG-bilayer structure can be also steered by the addition of further components. In particular, in MG systems containing water (*i.e.*, hydrogel and emulsion gels) the swelling of the layers and thus the water inclusion into lamellas is favored by the presence of ionic cosurfactants that cause electrostatic repulsions between the layers [43]. Commonly used co-surfactants are soy lecithin, diacetyl tartaric acid ester of MGs and diglycerides (DATEM), neutralized stearic

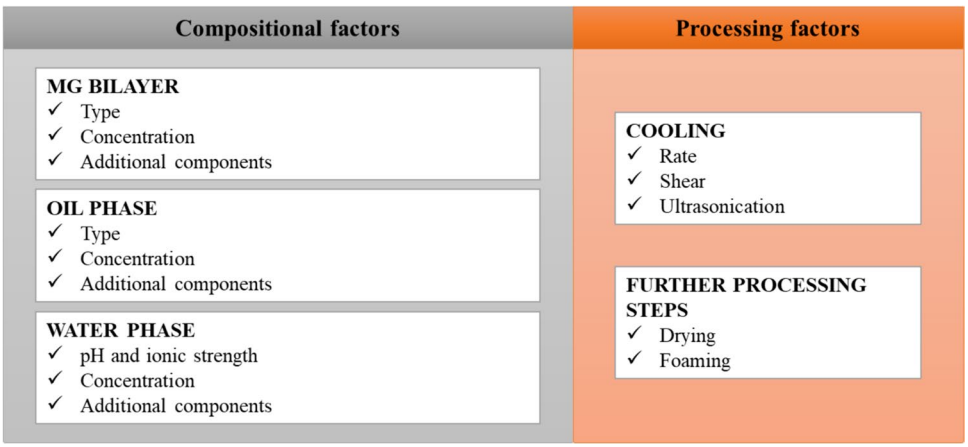


Fig. 1 Compositional and processing factors steering the structural properties of MG-based structures

acid and sodium stearoyl lactylate (SSL) [23, 27, 44]. The swelling behavior also depends on the pH of the aqueous phase, with high pH values inducing acid co-surfactant ionization, thus favouring MG lamellae swelling. For example, free fatty acids of commercial MGs are ionized at pH higher than 7. The pH is usually adjusted using NaOH but also other bases, either strong or weak, can be used [45].

Oil Phase

The nature of the oil phase was reported to significantly affect the structure of MG-based fat replacers containing oil [30, 46].

In particular, according to the used oil type, MG crystals with different morphologies were observed in MG-based oleogels. MG formed needle-like structures in cod liver, sunflower, extra virgin olive oil, and medium chain triglycerides (MCT) [35, 47–50] while larger spherulitic or rosette-like crystals were detected in corn and hazelnut oil [51, 52]. Moreover, Valoppi et al. [30] observed that higher oil viscosity favored gel network formation. However, castor oil-MG oleogel did not follow this trend, leading to impaired gel strength, due the high solubility of MGs in this oil [30].

In emulsified systems, the oil content should be also optimized. The oil content in O/W emulsion gels based on MGs cannot be increased beyond a specific threshold, depending on system composition in terms of water and MG content and ratio [40–42]. An increase of the oil fraction was only achieved by gently removing part of the water from the initial structured emulsion in the work of Calligaris et al. [24], where O/W HIPE with an oil content of 80 wt% was obtained. By contrast, W/O emulsion gels with an oil content as high as 80 wt% could be obtained by simply increasing the amount of disperse fraction in the formulation aided by the addition of a surfactant able to stabilize the water dispersed phase [53]. In both cases, such high dispersed phase concentration results in the deformation of the disperse phase droplet shape into polyhedra, separated by thin films of continuous phase, as well as in the enhancement of the gel-like behaviour, attributed to the close crowding of the dispersed droplets and to the high packing fraction [17].

Finally, the effect of minor components, including waxes, free fatty acids, oxidation products and antioxidants (e.g. tochopherols, polyphenols), cannot be underestimated [47, 54, 55]. For example, in the study of Alongi et al. [47], a role of polyphenols in enhancing the networking ability of MGs, based on their polar nature, was evidenced by the increase of oleogel rheological properties. Moreover, the addition of molecules able to gel the oil phase usually enhances the solid-like behaviour of MG-fat replacers. When applied to O/W emulsified systems, this approach leads to oleogel-in-water emulsion gels, recently reviewed by [56]. These systems can be obtained by adding other molecules besides MGs to structure oil, such as fats (e.g. anhydrous milk fat, or fully hydrogenated soybean oil, palm and palm kernel oil), waxes (e.g. rice bran, sunflower, candelilla and carnauba waxes) or ethylcellulose [42, 56].

Water Phase

The composition of the aqueous phase has been reported to strongly affect MG swelling capacity. In particular, the presence of cations and proteins strongly affects the swelling behavior of MG lamellas and thus water inclusion [23, 57]. The presence of Na^+ ions deriving from water dissociation of NaCl in the aqueous environment has been demonstrated to impair hydrogel stability, due to the Na^+ shield effect of the electrostatic repulsive forces induced by anionic surfactants between the MG bilayers [23]. A similar effect has been observed in the presence of proteins, which reduce MG networking ability, resulting in lower swelling [57, 58]. Valoppi et al. [45] found that concentrations of bases (e.g., NaOH) of at least 1 mM were required to obtain a proper swelling of MG layers in gelled emulsions. The addition of salts (e.g., NaCl), proteins (e.g., whey proteins), oligosaccharides (e.g., maltose, trehalose) and hydrocolloids (e.g., guar gam, xanthan gum) were instead found to interfere with the structural organization of MG multilayers in gelled emulsions [29, 39, 42]. Accordingly, the substitution of the aqueous phase with UHT skimmed milk, rich in proteins and salts, reduced the capacity of the system to form a stable emulsion, due to the ability of milk native components (such as proteins and ions) to compete with MG at the oil-water interface [58]. Contrarily, the addition of other surface-active ingredients, such as tea saponins, was effective in improving the rheological properties and the stability of the MG emulsion gel, which was attributed to the synergistical effect of saponins and MGs in interface stabilization. However, the saponin-to-MG ratio should be finely controlled to avoid opposite competitive effects leading to the destabilization of the emulsion structure [59]. Moreover, hydrocolloids such as proteins and polysaccharides can be added to gel the water phase, resulting in the formation of a bigel-type emulsion. By controlling the ratio between the water and oil phase, hydrogel-in-oleogel or oleogel-in-hydrogel systems can be obtained. For example, Cui et al. [60], Zheng et al. [61] and Zhu et al. [62], developed MG-bigels by adding chitosan, κ-carrageenan and gellan gum to water phase of a MG oleogel, respectively, begetting semi-solid materials with mechanical properties increasing with the oleogel fraction of the bigel. Similarly, Cui et al. [60] and Siachou et al. [63] exploited the gelling ability of gelatin in the production of MG-bigels with a protein-gelled water phase.

Processing Factors

Besides compositional factors, also processing parameters should be considered in the attempt of design MG-based structures. The cooling rate applied to cool down the system below the T_c of the MGs is the main factor to control. In fact, it defines the type of formed crystals, which affects the mechanical properties of the final MG structure, and the thermodynamic pathways of crystal transition, which affect system physical stability [64]. In the case of hydrogels, slow cooling rates (approximately 2 °C/min) resulted in a higher physical stability as compared to that obtained at higher cooling rate (10 °C/min). Slow cooling rates are in fact associated with longer time available for MG self-assembling into a fully hydrated lamellar structure [20]. On the opposite, oleogel structural properties and stability were found to increase with cooling rate in the range 0.67–1.09 °C/min [64]. Moreover, by increasing the cooling rate, a decrease of the onset temperature of gelation was observed [64]. This behaviour, also called supercooling effect, induces MG crystallization at temperatures below their actual crystallization temperature, due to the low time available for MG for self-organization in crystals [65]. Fast cooling rate after homogenization (> 6 °C/min) is also required for O/W emulsion gel formation. Slow cooling rates, in fact, result in a longer time spent by the material at high temperatures, at which flocculation and coalescence of the dispersed phase into larger droplets occurs, eventually leading to phase separation [39]. Moreover, the cooling rate is of particular importance when producing foamed systems [66]. In the case of oleofoams, high cooling rates of the unfoamed oleogel (4.3 °C/min) have been reported to be associated with higher oleogel foamability, due to the lower crystal dimension. Accordingly, low oleogel crystallization rates (0.5 °C/min) resulted in a decreased air incorporation ability, since jamming of large crystal at the air bubble surface is more difficult [67].

In any case, when dealing with systems containing oil, the holding time at high temperatures should be minimized as much as possible to reduce oxidation phenomena [47, 68, 69].

The application and intensity of shear is another pivotal factor during MG-system preparation. In the case of hydrogels and O/W emulsions, the application of shear during cooling could modify the water binding capacity of MG fat replacers [23]. In fact, shearing causes the disruption of the α-gel lamellar structure, favouring MG organization in a coagel (triclinic packed β-crystals), associated with water release from the MG bilayers and higher system hardness. This effect increases with the applied shear rate [20, 23, 70]. Also, oleogels obtained by static and sheared process exhibit different structures. Static conditions during crystallization are generally preferred to form firmer oleogels, since promoting the formation of junction zones among MG crystals [48]. On the opposite, shearing reduces network interactions and influences molecular alignment, leading to weaker oleogels [64, 71]. In this regard, Ojijo et al. [64] observed a reduced gelation of olive oil-MG mixtures stirred at 55 °C due to lamellar bilayer reorientation and formation of multilamellar vesicles that impair α-crystalline gel phase formation.

Shearing before cooling is required to produce O/W and W/O emulsion gels. The shear rate affects the dispersion level: as homogenization rate increases, the droplet size and distribution are reduced. Generally speaking, a reduction in particle dimension and polydispersity leads to higher physical stability of the emulsion. However, a higher number of smaller droplets also results in a higher interfacial area, requiring more MGs for stabilization [40].

Shearing is important also to steer the dimension and distribution of the air bubbles in MG oleofoam. For example, Brun et al. [34] subjected a MG-rapeseed oil-foam to shear and obtained the break-up of mother bubbles into daughter ones with a smaller size, associated with increased system stability. Nevertheless, excessive whipping leads to a decrease of overrun in both hydro- and oleo-foams with uneven bubble size distribution. This behaviour has been attributed to MG crystal bridging under shearing and subsequent bubble merging [37].

More recently, ultrasonication has been proposed as a strategy to tailor MG networking ability upon cooling. High intensity ultrasonication between 20 and 100 kHz applied to MG oleogels during the cooling step, induced the reduction of MG crystal size and led to stronger interactions among the MG crystals, eventually resulting in a reinforcement of the gel network [72, 73]. Similarly, Valoppi et al. [74] used ultrasounds to form dense bands of MG microcrystals, which acted as physical barriers in reducing the migration kinetics of a liposoluble colorant compared to statically crystallized oleogels.

In the attempt of producing MG HIPE, partial air-drying of O/W gelled emulsion could be conducted. Drying temperature and extent were found to be crucial processing parameters to avoid the breakdown of the system. In particular, temperatures lower than 30 °C and residual water higher than 20 wt% were found to guarantee structural integrity [24].

Finally, a foaming step is required to produce hydrofoams or oleofoams. The most commonly used device to prepare foams is a simple kitchen blender, which incorporates air bubbles and breaks them down to smaller dimensions as the foaming proceeds [21].

Food Design Using MG-based Structures as Fat Replacers

The implementation of MG-based structures as fat replacers in food formulations requires a proper design approach to guarantee the achievement of the technological, nutritional, and sensory properties of the target food.

Selection of the MG Fat Replacer

The first step of the design approach is based on the identification of the MG-structured systems that potentially best perform in relation to the intended food application. A first screening point could be based on the rheological/mechanical properties of the MG-based structures. In fact, although MG-based structures might exert considerably different rheological and mechanical properties depending on composition and nature/sequence of the steps applied during their preparation (Fig. 1), the firmness of the different materials can be compared based on a magnitude order scale. Figure 2 shows a schematic representation of the firmness of the different MG-based structured materials as compared to that of traditional fats. The figure also shows the firmness range of the fat needed for application in selected food classes.

The firmness ranges were estimated based on results reported in literature about rheological analysis of fats and MG-based structures. Based on the data shown in Fig. 2, depending on the intended food application, MG-based structures with properties as close as possible to those of the fat conventionally used in the formulation could be prioritized in the food design process.

For instance, fluid foods containing water as continuous phase, such as yogurt, creams and dressings usually contain lipid phase with low firmness. In these cases, hydrogels, hydrofoams, O/W emulsions and W/O emulsions can be possibly used in the formulations. Anhydrous dressings and creams are usually prepared with fluid-spreadable fats or butter and margarines which present firmness in a range comparable to that of emulsions and oleogels. Fats commonly used for the preparation of air-containg foods, such as mousses, include spreadable fats, butter, and margarines, presenting mechanical properties typically found in MG-hydrofoams and oleofoams. Since containing air, these

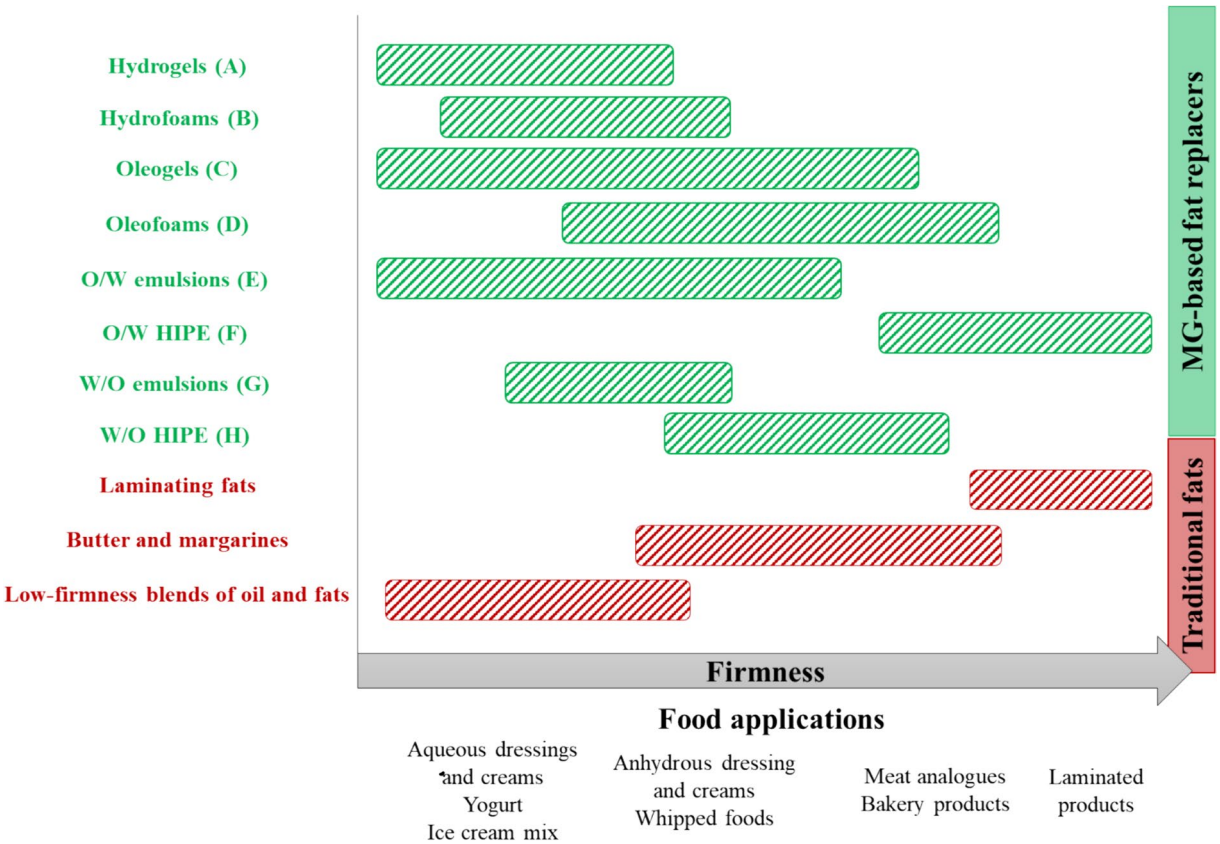


Fig. 2 Comparison of firmness range of MG-based fat replacers and traditional fats. The Figure also shows the food classes in which fat materials with the indicated firmness could be applied

MG-fat replacers can be used to substitute saturated rich fats while also reducing the overall caloric density.

The fats usually required for producing bakery products (e.g., biscuits, leavened products) and meat analogues are commonly represented by shortenings or margarines with a more pronounced firmness.

Oleogels as well as O/W emulsions can cover a wide firmness range and can be thus properly designed to mimic the behviour of semi-solid margarines and butter used in the preparation of meat analogues and bakery products.

Finally, the characteristics of laminated products, such as puff pastry, Danishes and croissants, are due to the presence of high-firmness laminated fats in the formulation. Such peculiar mechanical properties can be mimicked by MG-HIPE fat replacers. As compared to low-internal phase emulsion, in fact, HIPE present numerous interfaces and jamming of disperse phase droplets, accounting for rheological properties similar to those of laminating fats.

Analysis of the Performance of the Selected MG Fat Replacer

After a first selection of the MG-based structures has been performed, its actual performance should be assessed in the intended food. To this regard, Table 3 reports literature research works on the application of the different MG-based structures as fat replacers in different food categories, highlighting the effect of substitution on the lipid nutritional profile. Relevant articles were identified using Food Science and Technology Abstract, and Scopus database. For each reported study, the saturated fat reduction was estimated considering the formulation reported in the "Materials and Methods" of each publication. If not reported in the paper, SFA content was computed by consulting the USDA database [8].

According to the aim of substituting fats with MG fat replacers, in most cases, the substitution results in a significant reduction of SFA as compared to the standard product, which can also be associated with the reduction of the overall lipid content (Table 3). Although many MG-based structures are potentially applicable for the preparation of aqueous dressing and yogurts (Fig. 2), literature only refers to the application of hydrogels, which are suggested for the development of low calory products through total or partial substitution of lipids with a water-based system [22, 75]. In the case of ice cream mix, O/W gelled emulsion was also shown to be a suitable fat replacer. For the preparation of anhydrous products such as dressings and spreads, despite the potential applicability of different MG-based structures (Fig. 2), mainly oleogels have been studied so far, generally leading to a reduction of saturated fatty acids. Moreover, bigel-type emulsions have been proposed as milk cream analogues in the study of Cui et al. [60]. Despite the reformulation did not reduce the lipid content and the SFA, the developed bigel was claimed to be a sustainable plant-based alternative to dairy cream. In the field of meat analogues, the potential of MG-based fat replacers has been only scarcely explored. More specifically, Ferro et al. [76] have recently proposed the use of MG-based oleogels for 100% fat substitution in bologna sausages, leading to 93% reduction in saturated fatty acids. On the contrary, different MG-based structures have been studied as fat substitutes in bakery products (Table 4). These literature results indicate that the use of oleogels could allow the decrease of SFA in baked goods from 49 to 88%. By contrast, when O/W gelled emulsions were used, SFA can be decreased of about 90%, with a concomitant reduction in lipid content ranging from 40 to 56%.

Beside the nutritional aspect, the effect of substitution on technological and sensory properties should be carefully evaluated. For instance, in the study of Calligaris and coworkers [77], milk cream was successfully substituted with O/W gelled emulsion in ice-cream. The reformulated product was in fact characterized by a resistance to meltdown and structural collapse comparable to that of traditional ice-cream. Such desired behavior was attributed to the ability of MG lamellas surrounding sunflower oil droplets to favor the interconnection among air bubbles, stabilizing the ice-cream structure. In chocolate spreads, partial substitution of palm oil with an oleogel based on MG and pomegranate seed oil did not jeopardize the spread rheological properties, ensuring strong gel properties due to the tridimensional network formed between MG and palm oil [78]. Similarly, in filling-creams for sandwich cookies, the total substitution of beef fat with a high oleic sunflower oil-oleogel did not impair the rheological features, neither the adhesion between the cream and the cookies [28].

Various authors have shown that oleogels well-perform for the substitution of bakery shortenings and margarines [68, 79]. For instance, the presence of a sunflower oil-oleogel in muffin formulation guaranteed a higher leavening compared with the control sample containing margarine. Moreover, muffin crumb resulted more connected and homogeneous and oil migration during 10 days storage was reduced [68]. Similarly, cookies containing corn oil-oleogels instead of a traditional shortening, were characterized by hardness, color and thickness similar to those of the control [79]. The addition of a soybean oil-oleogel in bread acted as crumb softener, potentially inhibiting staling and enhancing product shelf-life. The softening effect of MG-oleogels was also confirmed in crackers and cookies [80, 81]. Similarly, the quality characteristics of sweet and white bread reformulated with a sunflower oil–water gelled emulsion were comparable to those of the palm oil-containing control [82, 83]. The use of this emulsion instead of palm oil also delayed bread staling, due to the well-known anti-staling properties of

Table 3 Examples of application of MG-based structures as fat alternative

Application	Substituted fat	MG-based structure	Composition of MG-based structure	Lipid content prior to substitution (wt%)	SFA content prior to substitution (wt%)	Fat substitution (wt%)	Amount of the MG-based structure in the final product (wt%)	MG content in the final product (%)	Estimated lipid content reduction (%)	Estimated SFA reduction (%)	Reference
Aqueous dressings and creams, yogurt, ice cream mix											
Ice cream	Milk cream	O/W gelled emulsion	Sunflower oil, water, co-surfactants	7	1.5	100	7	0.5	58	92	Calligaris et al. [77]
Dressing and mayonnaise	Spredable blends	Hydrogel	Water, co-surfactants	nr	nr	nr	nr	nr	nr	nr	Heertje and Hendricus [22]
Anhydrous dressing and creams, whipped foods											
Chocolate spread	Palm oil	Oleogel	Pomegranate seed oil	40	19.7	50	20	1	0	42	Fayaz et al. [78]
Filling creams	Beef fat	Oleogel	High oleic sunflower oil	22	2.5	100	26	2.6	0	23	Palla et al. [28]
Whipped cream analogue	Milk fat	O/W gelled emulsion (bigel)	Water, chitosan, MCT oil, co-surfactants	35	20	100	100	2.8	0	0	Cui et al. [60]
Meat and bakery products											
Bologna sausages	Pork fat	Oleogel	High oleic sunflower oil	20	19.3	100	20	1.0	0	92	Ferro et al. [76]
Muffin	Commercial margarine	Oleogel	High oleic sunflower oil	26	6.0	100	10	0.7–0.8	60	88	Giacomozzi et al. [68]
Cookies	Shortening	O/W gelled emulsion	Canola oil, water, stearic acid	21	5.2	100	21	0.9	40	91	Goldstein and Seetharaman [70]
	Shortening	Oleogel	Corn oil	20	13.0	100	20	0.6–3.0	0	79	Li et al. [79]
	Shortening	Oleogel	Soybean oil	13	3.9	100	13	1.3	0	77	Zhao et al. [81]
Short dough biscuits	Palm oil	O/W gelled emulsion	Flaxseed oil, water, co-surfactants	29	14.2	100	29	1.2	48	90	Anese et al. [84]
Sweet bread	Palm or sunflower oil	O/W gelled emulsion	Palm oil or sunflower oil, water; co-surfactants	19	9.6	100	42	0.4	56	92	Calligaris et al. [82]
White bread	Palm oil	O/W gelled emulsion	Sunflower oil, water; co-surfactants	7	3.5	100	12	0.3	40	93	Manzocco et al. [83]

Table 3 (continued)

Application	Substituted fat	MG-based structure	Composition of MG-based structure	Lipid content prior to substitution (wt%)	SFA content prior to substitution (wt%)	Fat substitution (wt%)	Amount of the MG-based structure in the final product (wt%)	MG content in the final product (%)	Estimated lipid content reduction (%)	Estimated SFA reduction (%)	Reference
Bread	Shortening	Oleogel	High oleic soybean oil	3	0.8	100	3	0.3	0	49	Zhao et al. [80]
Crackers	Shortening	Oleogel	High oleic soybean oil	8	2.2	100	8	0.8	0	49	Zhao et al. [80]
Laminated products											
Puff pastry	Laminating margarine	High internal phase emulsions	Water, sunflower oil, co-surfactants	22–40	8.2–14.8	100	37	2.3–5.2	18–20	64–80	Calligaris et al. [24]

If not reported in the paper, saturated fatty acid (SFA) reduction was estimated based on USDA database [8]

nr not reported since estimation was not possible, due to patented information, *MCT* medium chain triacylglycerols

MGs as well as to the interactions among starch, MG and oil [83]. Recently, MG-HIPEs have received particular attention for the production puff pastry as laminating palm margarine replacer. Although the reformulated puff pastry exhibited a lighter color and lower leaving capacity compared with the margarine-containing product, it showed comparable firmness and sensory friability [24].

Finally, it is noteworthy that not all MG-based structures shown in Table 2 have been applied as fat replacers in the development of low fat or low saturated fat foods. Indeed, literature on hydrofoams and oleofoams only deals with the development and characterization of these systems, without proposing an application. Therefore, an in-depth study to assess their applicability in food formulations is required to give information on the ability of these systems to replace fats in food structures containing air, which could take large advantage from the application of hydro- and oleofoams, when other MG-based structures do not allow an optimal performance.

Feasibility Assessment of the Selected MG Fat Replacer in the Target Food

Based on the information acquired in the previous steps of the food design approach, a MG-based structure likely suitable for the intended use can be identified. The performances of the selected MG fat replacer should be then assessed in the real food formulation. This step allows to understand the real technical feasibility of the MG-based reformulated product as well as to identify possible criticisms. Unfortunately, based on literature available to date, the complex interaction among the MG-based structures and the other ingredients is not easy to predict. In particular, the interaction of MG fat replacers with the other food ingredients may significantly alter food product processability. In this regard, changes in roll-out properties of bakery dough or in the flow behavior of dairy products and dressings may be expected, highlighting the strict relation between food product reformulation and process adjustment need. For instance, cookies prepared with O/W structured emulsion exhibited a different processability as compared to the control sample prepared with conventional shortenings, due to lower dough spreadability and firmness and higher break strength [70].

In addition, in some cases, formulation constraints may limit the use of MG fat replacers. In some products, to obtain the desired textural properties, a high amount of MG might be necessary. This is the case of products in which firm fats are traditionally used (Fig. 2), whose mechanical properties can be reached in MG fat replacers by increasing the MG content. Nevertheless, such high concentrations could be impossible to achieve, due to both law limitations and/or negative consumer perception.

Table 4 Main application as delivery systems of MG-based structures

MG based structure	Delivered compound	Functionality	Reference
Hydrogel	*Lactobacillus rhamnosus*	Protection during in vitro digestion	Melchior et al. [57]
Oleogel	Astaxanthin	Improved bioacessibility	Wang et al. [86]
	Curcuminoid compounds	Improved bioacessibility	Calligaris et al. [87]
	Lutein ester	Protection against UV irradiation	Jiang et al. [88]
	Hydroxytyrosol, tyrosol and α-tocopherol	Improved oxidative stability	Alongi et al. [47]
	Vitamin C	Improved oxidative stability	Wang et al. [89]
	Sesame oil flavour compounds	Controlled release in aqueous environment	Pang et al. [95]
O/W gelled emulsion	Curcumin	Controlled release in aqueous environment	Palla et al. [85]
	Limonene	Increased aroma entrapping capacity	Calligaris et al. [92]
	1-propanol, hexanal, diacetyl, limonene	Controlled release of flavor compounds	Mao et al. [93, 94]
	Lactobacillus rhamnosus	Protection during storage and in vitro digestion	Calligaris et al. [77], Marino et al. [90], Melchior et al. [57, 91]

Other Functionalities of MG-based Structures

Beside the effect in reducing fat and/or total saturated fat content of food, MG-based structures could offer further innovative advantages, especially related with the improvement of health functionalities (Table 4).

MG-based structures are particularly interesting as delivery systems due to the potentiality of the gel network to effectively protect bioactive compounds, probiotic cells, and other sensitive compounds (i.e. flavours) during food production and storage as well as consumption.

Oleogels and O/W emulsions have demonstrated to effectively protect a number of bioactive compounds against UV irradiation and high temperatures during storage not only in model systems but also in food prototypes such as margarine [47, 88, 89, 96]. Moreover, the peculiar structure of MG-based oleogels was associated with a lower oil in vitro digestibility due to the ability of the network to hinder the lipolysis [86, 87]. The structuration of oil droplets with MG crystals also allowed the controlled release of bioactive compounds during in vitro digestion as observed in the case of oleogels and O/W structured emulsion [85, 87]. In this regard Calligaris et al. [87] and Wang et al. [86] observed an increasing of bioacessibility (i.e. the fraction of ingested compound that is released from the food matrix thus becoming available for uptake by the intestinal mucosa) of curcuminoid compounds and astaxanthin upon in vitro digestion of MG-based oleogels.

Similarly, despite the reduced number of papers on this aspect, both hydrogels and O/W structured emulsion exhibited the ability to deliver probiotic bacteria. The presence of lamellar MG structures, near which cells were located, contributed to ensure microbial viability not only during processing and cold storage but also upon in vitro simulated digestion [57, 90].

Another application of MG-based structures consists in the release control of flavour compounds. Pang et al. [95] observed that the rigid crystal network of oleogels act as physical barrier hindering the liquid-vapour partition of sesame oil flavour compounds. A similar effect was observed in O/W emulsions whose structure greatly affected aroma partition improving the entrapping capacity [92]. The same systems containing Tween 20 as co-emulsifier were used to deliver flavour compounds exploiting the the affinity of flavour compounds to the different emulsion phases. Their release was affected not only by the MG lamellar structure, but also by the oil content and its nature [93, 94].

Closing Remarks and Future Perspective

Fat substitution in food in not a new challenge for both food scientists and industry managers. We assisted a progressive increase of efforts in designing fat alternatives over the last 20 years and the topic is still a point of attention for many scientists, considering the renewed boost generated by the increase attention on the food developments goals and the urgent need to favor the transition to more sustainable diets. Fat-containing foods are widely consumed in the diet of the population of many developed countries by all consumer categories, moving from babies to the elderly. They are considered traditional foods with an extraordinary capacity to deliver unique sensory properties and pleasure. For this reason, the transition to a healthier fat consumption is quite challenging and requires the assurance of the quality of the tasting experience.

Many strategies have been developed to re-balance the fat intake of the population, moving from educational and consumer-information policies to the taxation of high fatty foods or regulations on the reduction of TFA, up to the

reformulation of widely consumed products. The latter strategy might allow a "soft" transition to healthier foods while maintaining consumer pleasure during eating experience as well as consumer loyalty to food industry. However, food industry must be an actor of the game thrusting and investing in the transition, driven by consumer needs. This is exactly what is current happening considering the transition to a plant-based diet, with enormous efforts of all food chain actors in designing novel plant-based products mimicking animal ones. In this context, animal-fat replacement is still a great challenge due to the peculiarities of the structure of animal fats.

As reviewed in this manuscript, today, MG-based structures could be a reliable healthier alternative to saturated fats for the reformulation of food products. Thanks to the manifold possibilities in obtaining differently structured systems, a wide variety of food products could take advantage of this "flexibility" of usage. Moreover, from a technological point of view, the unit operations used to produce MG-based structures are already widely applied in the food industry (i.e. mixing, heating, cooling, foaming), with an easy-expected scaling up at a convenient cost. It must also be underlined that recent research attention has been dedicated to add further functionalities to MG-structured systems beside fat replacement. In particular, these systems can be loaded with a wide variety of compounds, ranging from vitamins, probiotic bacteria, and flavor molecules, which are protected during food processing and storage and released upon digestion with controlled kinetics. On the other hand, a point of attention is the possible aversion of consumers in the appearance of food additives in the ingredient list, despite a "*quatum satis*" usage of MG is allowed by food regulations. Moreover, the complex interplay between MG-based structures and the food matrix is still far from an exact science. For this reason, the comprehension of these aspects could open new opportunities in the usage of MG-based structures as fat replacers.

Author Contribution Sofia Melchior: Writing - Original Draft, Writing - Review & Editing, Visualization, Investigation, Methodology Stella Plazzotta: Writing - Original Draft, Writing - Review & Editing, Visualization, Investigation, Methodology Song Miao: Writing - Review & Editing. Lara Manzocco: Conceptualization, Writing - Review & Editing, Supervision. Maria Cristina Nicoli: Conceptualization, Writing - Review & Editing. Sonia Calligaris: Conceptualization, Writing - Review & Editing, Supervision.

Funding Open access funding provided by Università degli Studi di Udine within the CRUI-CARE Agreement.

Data Availability No datasets were generated or analysed during the current study.

Declarations

Competing Interest The authors declare no competing interests.

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