

Synergistic effects of oleogelators in tailoring the properties of oleogels: A review

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Abstract

Conventional solid fats play a crucial role as an ingredient in many processed foods. However, these fats contain a high amount of saturated fats and *trans* fats. Legislations and dietary recommendations related to these two types of fats set forth as a consequence of evidence showing their deleterious health impact have triggered the attempts to find alternate tailor-made lipids for these solid fats. Oleogels is considered as a novel alternative, which has reduced saturated fat and no *trans* fat content. In addition to mimicking the distinctive characteristics of solid fats, oleogels can be developed to contain a high amount of polyunsaturated fatty acids and used to deliver bioactives. Although there has been a dramatic rise in the interest in developing oleogels for food applications over the past decade, none of them has been commercially used in foods so far due to the deficiency in their crystal network structure, particularly in monocomponent gels. Very recently, there is a surge in the interest in using of combination of gelators due to the synergistic effects that aid in overcoming the drawbacks in monocomponent gels. However, currently, there is no comprehensive insight into synergism among oleogelators reported in recent studies. Therefore, a comprehensive intuition into the findings reported on synergism is crucial to fill this gap. The objective of this review is to give a comprehensive insight into synergism among gelators based on recent literature. This paper also identifies the future research propositions towards developing oleogels capable of exactly mimicking the properties of conventional solid fats to bridge the gap between laboratory research and the food industry.

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KEYWORDS

microstructure, oleogel, saturated fats, synergistic effect, *trans* fats

1 | INTRODUCTION

Solid fats play a vital role as an ingredient in various processed foods in providing rheological and sensory (flavor and texture) properties. Most of the solid fats that are used currently are manufactured through a conventional oil structuring technique called partial hydrogenation of vegetable oil. Solid fats produced through this technique (partially hydrogenated vegetable oils) are used as ingredients in a variety of foods such as shortenings and margarines, fried foods, baked products (crackers, doughnuts, and pies), and premixed products such as the pancake and hot chocolate mix (WHO, 2018a). A primary concern of these conventional solid fats is that they contain high levels of saturated fatty acids and industrially produced *trans* fatty acids (Puşcaş et al., 2020). The scientific evidence shows that these two types of fatty acids are strongly associated with many disease conditions (Astrup et al., 2020; Oteng & Kersten, 2020). Therefore, these fatty acids have received considerable critical attention from health professionals and food scientists. This has resulted in establishing diet-related recommendations and various legal regulations implemented in many countries in the past decades to minimize the use of these harmful fats.

A high intake of *trans* fat is positively associated with increasing the risk of death from a variety of causes. A systematic review has concluded that the consumption of *trans* fatty acids could cause a 34% increase in death by all causes, a 28% increase in the risk of death by coronary heart diseases, and a 21% increase in the risk of coronary heart diseases (de Souza et al., 2015). *Trans* fat increases the risk of cardiovascular diseases by increasing the levels of low-density lipoprotein cholesterol (LDL-C) and reducing the level of high-density lipoprotein cholesterol (HDL-C) (Co & Marangoni, 2018; de Souza et al., 2015). It is recommended that intake of saturated fats should be less than 10% of total energy intake and intake of *trans* fats less than 1% of total energy intake (FAO, 2010; Hooper et al., 2015; WHO, 2003). Due to the deleterious health effects linked with the consumption of *trans* fats, in 2015, the GRAS (Generally Regarded as Safe) status for the partially hydrogenated oils has been revoked by the US Food and Drug Administration (US FDA) (US FDA, 2018). Further, WHO has released a step-by-step guide, called the “REPLACE action package” with the target of total elimination of industrially produced *trans* fats from global food supplies by 2023 (WHO, 2018a). Saturated fatty acids are

also known to be linked with increasing the risk of cardiovascular disease by increasing the levels of LDL cholesterol (Jakobsen et al., 2009). Therefore, the demand to lessen or remove saturated fatty acids and *trans* fatty acids from the human diet is the driving force for the development of oil structuring to find promising alternatives for partially hydrogenated vegetable oils.

Presently, a novel oil structuring technique, called oleogelation, is gaining mounting interest in the food industry as a promising alternative to conventional partial hydrogenation technique to produce healthy gels that mimic solid fats. It is a physical method to convert liquid oils into gels (oleogels) without changing the chemical characteristics of oil (Luo et al., 2019). By definition, oleogelation is the process of making oil-based continuous gels in which gelator/s (oleogelator or structurant) immobilizes liquid oil within a structured three-dimensional network (Wijarnprecha et al., 2019). Even though the research on oleogels has a long history in nonfood applications such as analytical chemistry, material science, drug delivery (Kumar & Katare, 2005; Murdan, 2005), and cosmetics (Aiache et al., 1992; Patel, 2017), its focus in food applications is a new topic. Oleogelation has been reported in the literature since the late 1950s (Fedotova & Trapeznikov, 1958a, b). In the last 10 years, there has been a substantial raise in the number of publications related to the food applications of oleogels because of their promising benefits. Oleogels can confer the distinctive properties of solid fats with reduced saturated fatty acids and zero *trans* fatty acids (Calligaris et al., 2020; O’Sullivan et al., 2017) and can have increased stability and shelf-life. Moreover, the delivery of bioactive compounds is an additional benefit of these novel fat alternatives (Martins et al., 2018).

The saturated and *trans* fatty acids present in the solid fats are responsible for their functionality, that is, they provide a unique mouth feel, hardness, texture, crispiness, and spreadability to the solid fats (Co & Marangoni, 2018; Patel, 2015). Therefore, reducing and eliminating saturated fatty acids and *trans* fats, respectively, without affecting their functionality in solid fat is quite challenging. Triacylglycerol forms of these fatty acids create a “fat crystal network,” which is an assembly of a colloidal or supracolloidal particle network. This network cause structuring of the fat into a solid or solid-like material. Therefore, the fundamental principle of alternative edible oil structuring of reducing or eliminating saturated fats and *trans* fats means there should be an alternative network for this specific crystal

network structure (Co & Marangoni, 2018). A variety of oleogelators have been researched and reported to exhibit the potential to form a crystal network that can mimic the properties of solid fat.

Although a high volume of previous works has paid attention to making oleogels intended for food application from different edible oils using different gelator molecules, still oleogels have not attained the exact properties of conventional solid fats. Therefore, creating the specific crystal network to achieve the required properties of solid fat remains the primary challenge in developing oleogels for food applications (Aguilar-Zárate et al., 2019; Flöter et al., 2021). One of the important aspects controlling the network structure and the resulting properties in the oleogels is the oleogelators. Much of the earlier works focused primarily on the use of single oleogelators to make oleogels (monocomponent oleogels). However, the use of combinations of oleogelators to make oleogels (multicomponent oleogels) has been the focus of several recent published works, and most of these studies demonstrated the existence of synergistic interactions among different oleogelators (synergistic effects of oleogelators mean that the properties of a multicomponent gel developed using a combination of gelators are superior to their corresponding monocomponent gels) (Abdolmaleki et al., 2020; Barroso et al., 2020; Eisa et al., 2020; Gaudino et al., 2019; Lopez-Martínez et al., 2015; Okuro et al., 2018; Winkler-Moser et al., 2019; Shuaishuai Yang et al., 2020). Therefore, establishing the synergism among gelators will pave the way to tailor the oleogels to cater the food industry with a promising healthier solid fat alternative. There are many excellent reviews and book chapters published recently with the major focus on the fundamentals of oleogelation (Bascuas et al., 2021; Davidovich-Pinhas, 2019; Hwang, 2020; Okuro et al., 2021; Pakseresht & Mazaheri Tehrani, 2020; Patel, 2017; Singh et al., 2017; Zhao et al., 2021) and potential food applications of oleogels (Martins et al., 2018, 2020; Pehlivanoglu et al., 2018; Scharfe & Floter, 2020). Few reviews have lightly touched the synergism of oleogelators (Hwang, 2020; Patel & Dewettinck, 2016). Even though very recently, there is an escalation in the number of papers published on multicomponent gels exploring the synergism of oleogelators, there are no reviews emphasizing the synergism of oleogelators to produce tailor-made oleogels. Since investigating the synergism of oleogelators is a continuing concern in the tailoring of lipids, this paper reviews the synergistic effects of oleogelators in structuring the oleogels based on the works published in the last 5 years. This review considers only the works intended for food applications and done without the use of solvents (because the use of organic solvents limits their applicability in foods). This paper also identifies the gaps in the knowledge on tailoring oleogels to provide an insight to researchers on

their future research focus towards connecting the science and the food industry. The initial sections of this review are structured to provide an overview of oil structuring with a major focus on comparing the mechanism of formation of traditional solid fats and oleogels, types of oleogelators, mechanism of oleogelation, and the general methods used in characterizing oleogels. Then, the paper reviews the synergistic combinations of oleogelators used in the structuring of various edible oils based on recent literature. Finally, the paper closes with identified gaps in the knowledge on developing oleogels for food applications and the propositions for future research.

2 | OIL STRUCTURING: CONVENTIONAL AND NOVEL APPROACHES

Oil structuring is an approach to make semisolid or solid-like fats from liquid oils. The crystallization process of conventional solid fats involves the temperature-induced formation of fat crystals by chemical or physical bonds between the triacylglycerols. The triacylglycerol molecules self-assemble into lamellar crystals (crystalline nanoplatelets), which further interact through one-dimensional packing to create the final structure of solid fats containing clusters of crystals (Davidovich-Pinhas et al., 2016). The presence of a large proportion of high melting point triacylglycerols (saturated and *trans* fats) provides semisolid nature for these fats (Mattice & Marangoni, 2019). The molecular structure of triacylglycerols, principally, the long aliphatic chain, get packed into various structures during solidification (crystallization in a space-filling three-dimensional lattice) in different polymorphic forms (α , β' , and β), which contribute to the functional properties of the resulting fat system (Devi & Khatkar, 2016; Flöter et al., 2021; Moorthy, 2018).

Traditional solid fats are manufactured using partial hydrogenation of vegetable oils. During partial hydrogenation, some of the unsaturated fatty acids present in *cis*-form can be converted into *trans*-form, leading to a high amount of *trans* fatty acids (industrially-produced *trans* fats). In addition, solid fats contain a high amount of saturated fatty acids. Because of evidence showing adverse health effects associated with these two types of fatty acids, exploring alternate oil structuring techniques has begun by the researchers in the early 20th century aiming to minimize saturated fatty acids and eliminate *trans* fatty acids from the human diet. *Trans* fatty acids are produced industrially during processing, and therefore, their total or effective elimination is feasible. In contrast, saturated fatty acids are unavoidable in the diets, and they cannot be entirely removed from the diet, however, could be minimized (Co & Marangoni, 2018).

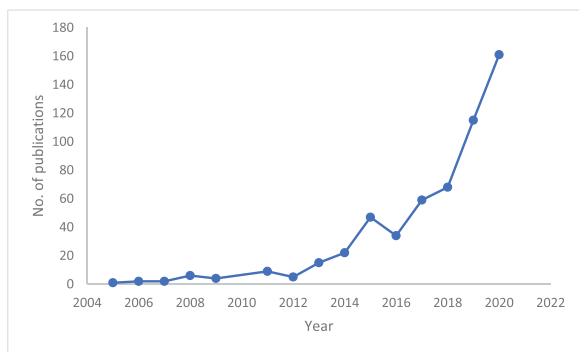


FIGURE 1 Number of publications on oleogels from the year 2005 to 2020

Since saturated fatty acids and *trans* fatty acids are important in solid fats for their functionality as they provide the specific network structure to the product, any solid fat alternative without *trans* fatty acids and reduced saturated fatty acids must have a unique structure that can impart (mimic) the properties of conventional solid fats. In this venture, oil structuring techniques (structuring the liquid oils into a solid or solid-like material) such as fractionation and interesterification have been developed. Among these two, interesterification (chemical or enzymatic) is considered a promising technique (Puşcaş et al., 2020). Chemical interesterification uses chemicals and needs severe processing conditions (Sivakanthan & Madhujith, 2020). Enzymatic interesterification does not need any chemicals and could be carried out under mild conditions; however, the high cost of enzymes may limit their application in foods (Puşcaş et al., 2020). Compared to interesterification, oleogelation is relatively new in the field of food applications.

3 | OLEOGELATION AND OLEOGELS

Oleogelation is an oil structuring method that transforms liquid oil into a gel using solids called oleogelators (structurant or gelator) which entrap the oil by forming a three-dimensional gel network. Oleogels are a subclass of colloidal structures called organogels. Oleogel is defined as a gel system containing liquid oil (continuous phase) entrapped or immobilized in a three-dimensional network of self-assembled molecules of a gelator or a mixture of gelators (Patel, 2018a). In the past few years, oleogelation has become a hot topic in the field of lipid research for healthy food applications. The number of publications resulting from the search of term “oleogel*” in the “topic” in the database Web of Science core collection is shown in Figure 1, which demonstrates the rapid progress in the scholarly work on oleogels. Much of the research focus

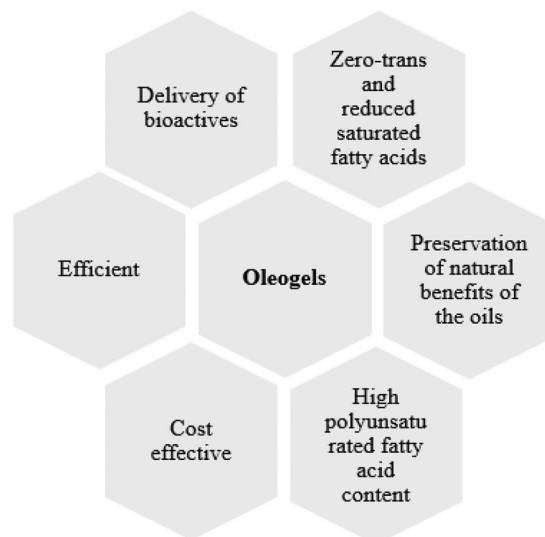


FIGURE 2 Advantages of oleogels related to food applications

on oleogelation is towards altering the microstructure of oleogels through a variety of mechanisms such as using a variety of gelators, using the combination of gelators, using different oil types, and modifying the processing parameters.

Oleogels possess many beneficial aspects (Figure 2). The primary characteristic of the oleogels is that they can be developed with zero-*trans* and reduced saturated fats, which make oleogels a healthier fat compared to conventional solid fats. This process does not require any chemical or structural modifications in the triacylglycerol molecules. Therefore, the content of unsaturated fatty acids and original regiospecific positioning of the fatty acids in the glycerol backbone remain unchanged, which helps preserve the inherent nutritional qualities of the oil used. Therefore, in simple terms, oleogels are physically structured oils with solid-like attributes and with the same nutritional quality as liquid oil (Guo, Cai, et al., 2020; Silva et al., 2021). In addition to containing zero-*trans* and reduced saturated fatty acid contents, the oleogels can be made to contain high polyunsaturated fatty acid contents which are associated with a plethora of beneficial health effects, and this is not possible in the case of conventional solid fat development by partial hydrogenation because the crystallization process does not primarily rely on the degree of saturation of the oil in oleogelation. Furthermore, from a nutritional standpoint, oleogels can be used as a means of delivery of bioactive compounds (Pinto et al., 2021). A few examples of the bioactive compounds that are studied with oleogels include curcuminoids (Calligaris et al., 2020; Li et al., 2019) and β -carotene (O’Sullivan et al., 2017; Zheng et al., 2020). Moreover, oleogelation is considered an efficient technique because the gelators

can efficiently entrap more than 90% (w/w) of oil at low concentrations (Patel, 2018a).

Seminal reviews published by (Co & Marangoni, 2012; Dassanayake et al., 2011) provide clear perspectives on the fundamentals of oleogelation which involves different routes of network formation such as crystalline particles, self-assembled networks, and polymer networks (Flöter et al., 2021). Even though oleogelation includes some mechanisms occurring during conventional solid fat formation such as nucleation, crystal growth, aggregation, and network formation, the crystal morphology, crystal size, and crystal growth patterns are different in oleogelation and traditional solid fat formation. In oleogelation, the unidirectional crystal growth and less tendency for crystal aggregation enable the network formation at less proportion of crystalline phase (Patel & Dewettinck, 2016).

Monocomponent oleogels are produced using only one oleogelator, while multicomponent oleogels are produced using two or more oleogelators or a combination of gelator/s and nongelling additive/s. Multicomponent gels usually offer more advantages compared to monocomponent gels. In the case of making monocomponent gels, a comparatively high amount of single gelators (sometimes up to 30% by weight) is typically needed for oleogelation. Further, research has revealed that monocomponent oleogels in most cases lack in properties of conventional solid fats. Nevertheless, the mixture of oleogelators can form an enhanced gel network by modifying the functional arrangements of molecules and positive interactions. This improved gel network can entrap a high amount of liquid oil, thereby decreasing the amount of gelators (in most cases, 1–10% by weight) needed to provide the desired texture to the oleogels (Callau et al., 2020; Martins et al., 2019; Okuro et al., 2020; Pakseresht & Mazaheri Tehrani, 2020).

3.1 | Oleogelators

In the case of conventional solid fats, the functionalities such as unique texture, oil binding, rheological properties, and stability are provided by saturated fats and *trans* fats. Therefore, in the oleogels, these functionalities should be imitated by nonfat structuring agents called oleogelators or gelators or structurants (Patel, 2018a).

Oleogelators used for food applications must be food grade, should not have any adverse effect on sensory qualities of the oleogel, and should be economical at the concentrations used and the resulting oleogel should exhibit properties similar to conventional solid fats. Various materials that show good oil structuring abilities such as monoglycerides, phytosterols, waxes, and so forth, are already approved as food additives (US FDA, 2011). The strong gela-

tion capacity of oleogelators is another key factor in the selection of oleogelators because this property will enable to attain the properties of food products with less amount of the gelator, subsequently, reducing their impact on the sensory properties of the resulting oleogels (Choi et al., 2020).

Figure 3 illustrates different types of oleogelators reported in the literature with examples. Based on molecular weight, oleogelators can be categorized as low molecular weight oleogelators (molecular weight of <3000) and high molecular weight oleogelators. Low molecular weight oleogelators are relatively small molecules such as monoglycerides, natural waxes, wax esters, ceramides, hydroxylated fatty acids (12-hydroxystearic acid and ricinelaic acid), lecithin, phytosterols, and oligopeptides (Patel, 2018b; Scholten, 2018). Monoglycerides, waxes, and sphingolipids are used in monocomponent gels (Patel, 2015) and are crystalline particles. Polymers (proteins and polysaccharides) are used as high molecular weight oleogelators. Examples for polymers that are researched in oleogelation include polysaccharides such as ethylcellulose (Davidovich-Pinhas et al., 2015a, b), hydroxypropyl methyl cellulose (Meng et al., 2018; Patel et al., 2015), pectin (Luo et al., 2019), chitin (Nikiforidis & Scholten, 2015), xanthan gum, guar gum (Abdolmaleki et al., 2020), kappa-carrageenan (Plazzotta et al., 2019), alginate, hyaluronic acid and chitosan (Silva et al., 2021), and proteins such as gelatin, caseinate, soy protein isolate, and β -lactoglobulin (Feichtinger & Scholten, 2020). Most of the low molecular weight oleogelators can gel oils at low concentrations (3%, w/w) or lower. For example, it is reported that the minimum sunflower wax concentration required to form gel in five different edible oils ranged from 0.3 to 1% (Hwang et al., 2016). Another study has shown that the minimum concentration of sunflower wax, tea wax, rapeseed wax, orange peel wax oleogel, rose wax, and berry wax to form gel in sunflower oil were 1.0%, 7.0%, 25.0%, 15.0%, 8.0%, and 5.0%, respectively (Yilmaz et al., 2021). However, generally, a minimum of 20% solid fat is needed to exhibit the rheological properties of a solid (Co & Marangoni, 2018).

Figure 4 illustrates the relative proportions of publications that resulted for the search of ((TS = (Oleogel)) AND TS = ("Name of gelator")) NOT DT = (Review) in the database, Web of Science (the search was performed on September 15, 2021). From this, it is obvious that the waxes are the most extensively researched group of oleogelators due to the desired textural properties of resulting oleogels that can be achieved with a small amount of waxes (Blake et al., 2014; Martins et al., 2018).

Waxes are lipophilic organic compounds composed of long alkyl chains (>16°C) and typically contain functional groups such as carboxyl, hydroxyl, ketones, aldehydes, and esters (Scharfe & Floter, 2020). However, waxes from

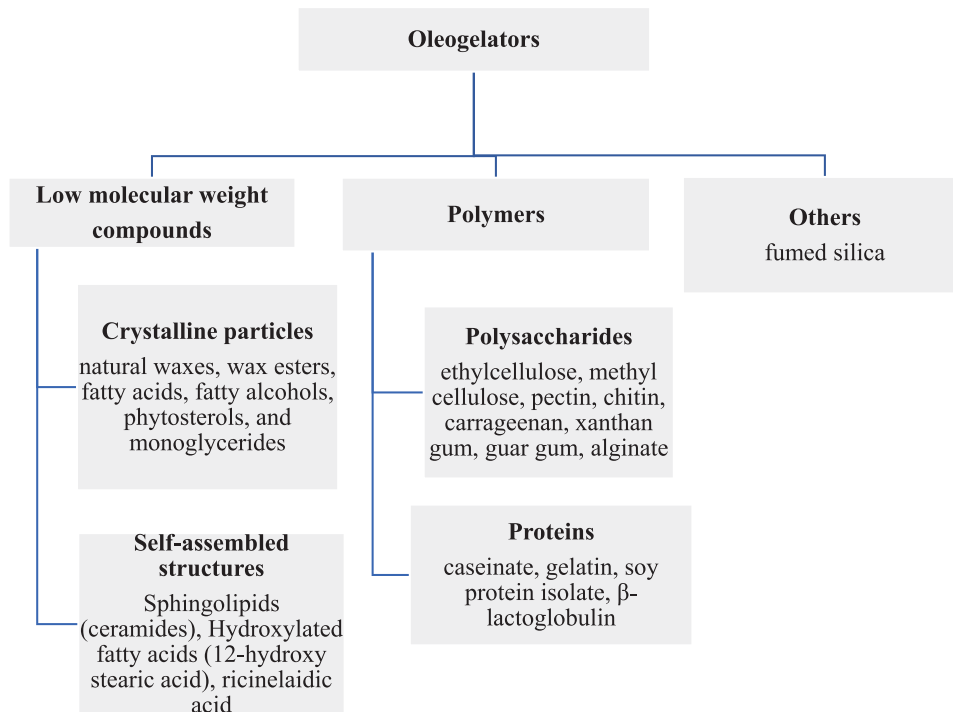


FIGURE 3 Types of oleogelators

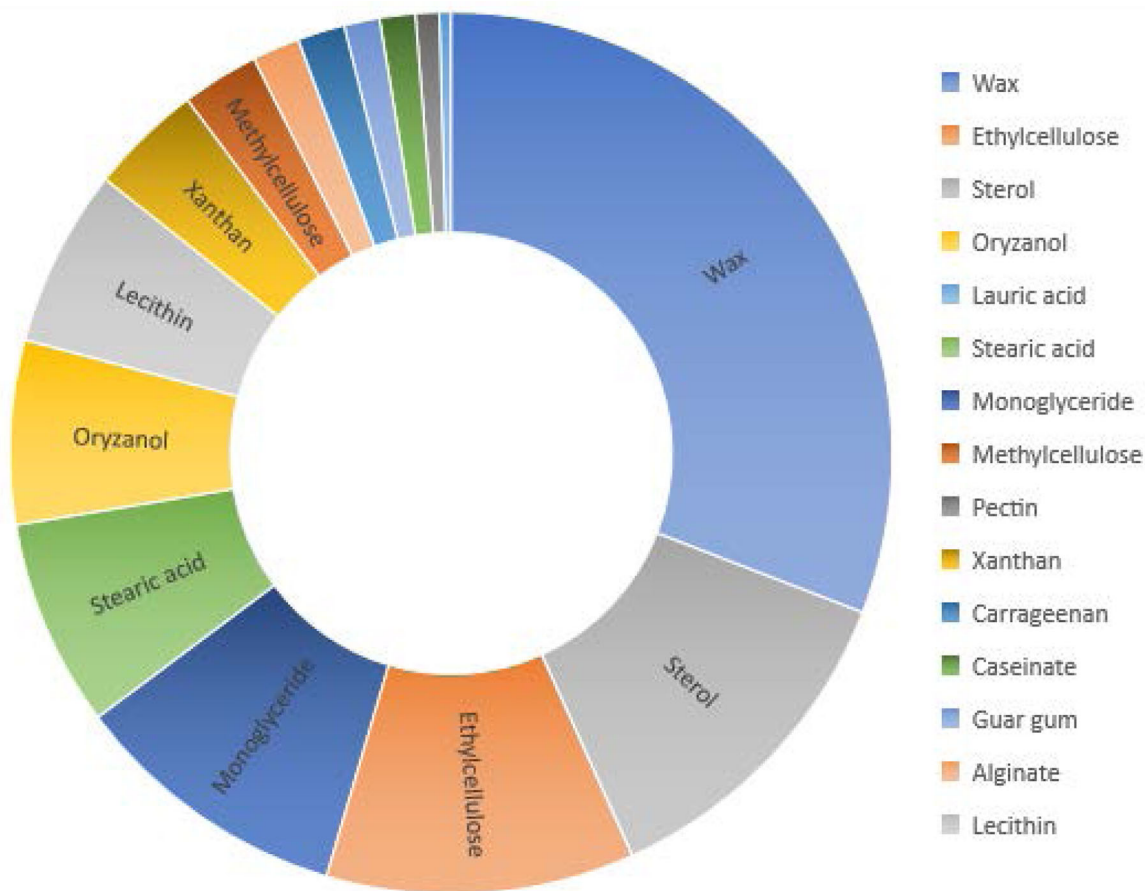


FIGURE 4 Relative proportions of articles published on oleogel development using different gelators based on literature search in Web of Science

different sources may differ in their chemical composition, which influences the melting and crystallization properties, gelation points, and crystal structures. For example, the glycerides of short chain fatty acids result in a low melting temperature, whereas the waxes containing mainly comprised of long chain fatty acids and fatty alcohols have a high melting point (Barroso et al., 2020). An important drawback in using waxes as oleogelators is the waxy mouthfeel of the product. It limits the amount of wax used in gelling intended for food uses. Moreover, oleogels developed using waxes have elevated melting temperatures compared to traditional solid fats, which could lead to an unattractive waxy mouthcoating. Using binary mixtures of wax shows the eutectic behavior of two waxes (Choi et al., 2020). Examples of most extensively studied waxes include sunflower wax (Barroso et al., 2020; Tavernier, Doan, et al., 2017a; Winkler-Moser et al., 2019), rice bran wax (Tavernier, Doan, et al., 2017a), carnauba wax (Shuaishuai Yang et al., 2020), bees wax (Fayaz et al., 2017; Gómez-Estaca et al., 2019; Martins et al., 2017; Pang et al., 2020; Ristani et al., 2018; Winkler-Moser et al., 2019), candelilla wax (Winkler-Moser et al., 2019), berry wax (Barroso et al., 2020; Tavernier, Doan, et al., 2017a), and fruit wax (Okuro et al., 2018).

Next to the natural waxes, phytosterols, especially β -sitosterol is widely studied. From the nutritional point of view, β -sitosterol has gained attention due to its ability to reduce blood cholesterol (Arjen Bot & Flöter, 2018). Furthermore, they have the ability to structure oil, and these two properties make β -sitosterol a good candidate for oil structuring. Ethylcellulose is a polymer derivative of cellulose. It is also highly researched due to its potential to be dispersed directly in liquid oil and the resulting gelation capability (O'Sullivan et al., 2017).

Monoglycerides are another group of oleogelators that can be used to make oleogels. Few examples for the use of monoglycerides in oleogels include monostearin (Wei & Huang, 2019; Yu et al., 2012) and mixture of monostearin and monopalmitin (Ojijo et al., 2004). However, the monoglycerides are usually complex mixtures of acylglycerides and different mixtures may have different proportions of the compounds (Bin Sintang et al., 2017; Giacomozzi et al., 2019). Therefore, they may exhibit different gelling abilities depending on their composition and the type of oil.

Stearic acid and its derivatives such as 12-hydroxy stearic acid and stearyl alcohol are also extensively studied in oleogelation. Stearic acid is a saturated fatty acid (C18:0), and it is the second most abundant fatty acid in nature next to palmitic acid (C16:0) (Sagiri et al., 2015). Unlike many other long chain saturated fatty acids, stearic acid is not associated with increasing the risk of atherosclerosis, but it helps reduce LDL-cholesterol (Senyilmaz-Tiebe et al., 2018). Moreover, stearic acid has good gelation proper-

ties attributed to its long aliphatic chain (Uvanesh, Sagiri, Senthilguru, et al., 2016). Due to these reasons, stearic acid can be considered a good candidate for edible oil structuring. The presence of hydroxyl group in 12-hydroxy stearic acid provides polarity to the molecules and favors the development of emulsion oleogels. In hydrophobic gels, the presence of polar groups enhanced interfacial tension between edible oil, and the gelators result in poor stability of resulting gels. Therefore, the use of stearic acid could improve the stability of anhydrous oleogels (Sagiri et al., 2015).

Oryzanol is a plant sterol ester present in rice bran oil. Similar to the phytosterols, oryzanol also has additional nutritional benefits such as reducing serum cholesterol levels (Scharfe & Floter, 2020). Lecithin itself cannot form a gel; however, it is a well-known crystal habit modifier (Guo, Song, et al., 2020) and is extensively studied in combination with other gelators such as ethylcellulose (Aguilar-Zárate et al., 2019), sucrose esters (Sintang et al., 2017), fruit wax (Okuro et al., 2018), oryzanol (Matheson et al., 2017a), α -tocopherol (Nikiforidis & Scholten, 2014), stearic acid (Gaudino et al., 2019), and ceramide (Guo, Song, et al., 2020). The use of polymer gelators for oil structuring is relatively new compared to the low molecular weight oleogelators. Proteins and polysaccharides have been shown to have the ability to form gels; however, their mechanism of formation of gels is different from the mechanism of low molecular weight oleogelators. Low molecular weight oleogelators are lipophilic and can be directly dispersed into the oil to form gel network via physical interactions such as Van der Waals, hydrophobic, and hydrogen bonds between the small molecules. Most of the proteins and polysaccharides are hydrophilic in nature, and therefore they cannot be directly dispersed into the oil for making oleogels. Therefore, different indirect approaches such as emulsion-templated methods have been developed to make oleogels using polymer gelators. The proteins and polysaccharides form three-dimensional network with visco-elastic properties via physical interactions such as hydrogen bonds (Davidovich-Pinhas, 2019).

Nowadays, the use of combinations of oleogelators and the use of nongelling additives together with oleogelator to enhance the gelation and resulting properties of oleogels are of increasing interest currently. Some examples include combinations of fatty alcohols and fatty acids (stearic acid and stearyl alcohol) (Gravelle, Blach, et al., 2017a), phytosterols and sterol esters (γ -oryzanol and β -sitosterol) (Fayaz et al., 2021; Moschakis et al., 2016), and phytosterols and fatty acids (Shu Yang et al., 2017, 2018). The combination of β -sitosterol and γ -oryzanol has got great interest in oleogelation not only because of their gelation capacity but also due to their positive effect on lowering blood cholesterol levels (Scharfe & Floter, 2020).

4 | METHODS OF OLEOGELATION

Based on the strategy used to disperse the structurant in the oil, the methods of oleogelation are classified into two categories such as direct method and indirect method. Lipophilic structurants such as triacylglycerols, fatty acids, fatty alcohols, and waxy esters are used in oleogelation via a direct method, that is, oleogelator is dispersed into the liquid oil followed by heating above their melting temperature and subsequent cooling to form gels. So far, only one food polymer called ethylcellulose (a linear hydrophobic derivative of cellulose) among many others is known to form gel liquid oil via direct dispersion (Patel, 2015). Its gelling ability by direct dispersion is attributed to its hydrophobic nature and semicrystalline characteristics (Davidovich-Pinhas et al., 2015a).

The studies on using polymers in oil structuring are not as many as studies on low molecular weight oleogelators. Most of the natural polymers are hydrophilic and therefore cannot be dissolved in the oil by direct dispersion (Feichtinger & Scholten, 2020). However, polymers (except ethylcellulose) can form a gel network through a multi-step indirect process called templating method (emulsion template or foam template). Emulsion-templated method is considered to be an efficient indirect method. It is a multistep process consisting of dispersing the oleogelators in the oil, adding water gradually while stirring followed by homogenization. Due to their surface-active properties, the gelators accumulate at the oil–water (emulsion template) or air–water (foam template) interfaces. The subsequent removal of the aqueous phase leaves the dried matrix of the polymer (emulsion templates) or a porous architecture of polymer which contains liquid oil entrapped (foam templates) (Luo et al., 2019).

4.1 | Mechanism of oleogelation

The mechanism of oleogelation means how the network structure is formed during oleogelation by any method (direct or indirect). The understanding of the mechanism behind the gelation of edible oils is quite complicated (Patel, 2017). Few excellent reviews on the mechanism of the formation of gels from edible oils have been published (Martins et al., 2018; Patel, 2017). The mechanism of oleogelation depends on the method (direct or indirect) employed. When low molecular weight compounds are used (direct methods), the network structure is formed by crystalline particles (when lipid-based gelators such as fatty acids, waxes, and monoglycerides are used) or self-assembled structures. In the case of indirect methods, self-assembled structures of polymers or polymeric strands form the network structure (Puscas et al., 2021).

When low molecular weight oleogelators are used, there are three stages involved in the formation of gels such as formation of primary particles (nucleation), self-assembly, and self-organization (Figure 5). The primary particles are formed through precipitation and/or crystallization induced by weak solute (gelator)–solvent (oil) interaction. In the second step, individual particles are assembled into crystalline particles such as fibers, ribbons, platelets, rods, or tubules (Figure 6a–f), and the molecular assemblies/clusters are stabilized by hydrogen bonding, electrostatic, and Van der Waals interactions and pi stacking. In the final step, a continuous network (supramolecular structure) is formed by anisotropic growth and anisotropic diffusion, and the oil is immobilization in a three-dimensional network due to the interactions between particles (Callau et al., 2020; Patel, 2017).

In most cases, oleogelators form mesoscale structures, which do not grow to the same magnitude in three dimensions (asymmetric structures). When the growth of oleogelator is limited to one dimension fibrillary. A needle-like mesoscale structure is formed, whereas if growth occurs in two dimensions, a platelet-like structure is formed (Co & Marangoni, 2012). Generally, the low molecular weight oleogelators such as monoglycerides and plant-based waxes self-assemble into a three-dimensional crystalline network through noncovalent interactions, building space-spanning networks, and resulting in thermoreversible gels and thus the resulting oleogels have a structure similar to that of traditional fats. Even though the saturated monoglycerides are effective in forming three-dimensional networks similar to saturated triacylglycerols, since they have health effects similar to saturated fatty acids, the use of these compounds in oil structuring cannot be considered superior to conventional structuring in terms of health effects (Co & Marangoni, 2018; Feichtinger & Scholten, 2020; Scharfe & Floter, 2020). However, the application of unsaturated monoglycerides can overcome such issues. For instance, enzymatically synthesized unsaturated 2-monoglyceride has been used to make oleogel from soybean oil (Chen et al., 2021). The studies focusing on using unsaturated monoglycerides are very limited. Some oleogelator molecules such as phytosterols and oryzanol form larger structures (tubules) (Moschakis et al., 2016) or one-dimensional fibers such as 12-hydroxystearic acid.

The high molecular weight gelators such as polymers form gel either via direct dispersion of the structurant into the liquid oil (ethylcellulose) or through an indirect approach (templating) (Gravelle, Davidovich-Pinhas, et al., 2017b). When the ethylcellulose is heated beyond its glass transition temperature (140°C), the unfolding of the molecule structure leads to partial solubilization of the ethylcellulose in the

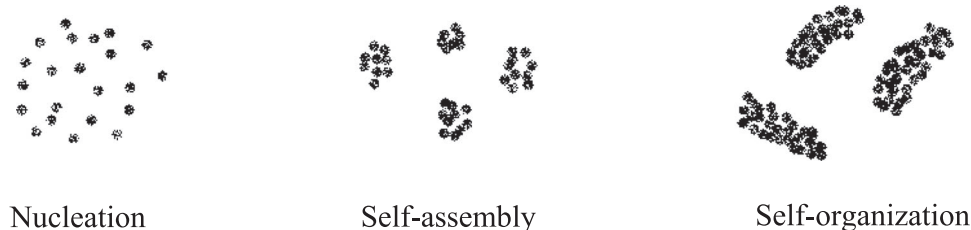


FIGURE 5 Schematic presentation of the mechanism of oleogelation by low molecular weight oleogelators

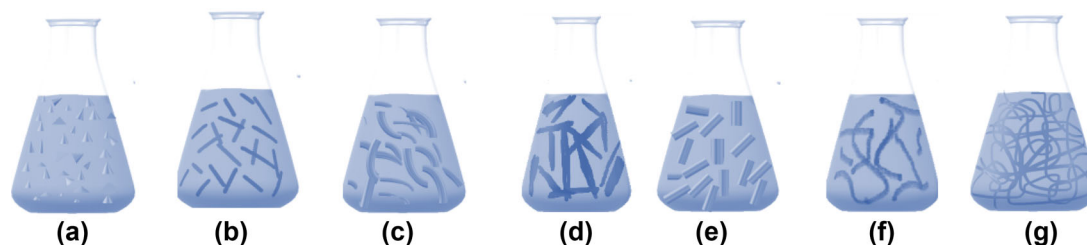


FIGURE 6 Assembly pattern of crystals; (a) crystals, (b) fibers or needle-like, (c) tubules, (d) platelets, (e) rods, (f) ribbons, and (g) polymer strands

oil. The subsequent cooling will stimulate the inter-polymer hydrogen bonds between the free or available (unsubstituted) hydroxyl groups of the polymers to produce a three-dimensional polymer network with the capability to entrap liquid oil (Martins et al., 2018; Wang et al., 2016).

Other polymers are used in oleogelation via oil-in-water emulsion templates stabilized by the polymer. In this approach, the polymers get hydrated to form extended and open conformations (Figure 6g), which facilitate stronger molecular interactions with the liquid oil. The hydrated polymer conformations overlap, leading to the formation of junction zones which consequently results in the gelation of the aqueous phase. The removal of water will leave behind the dried microstructures with entrapped liquid oil. The interfacial layer in the network should be robust enough to resist dehydration during drying. This could be achieved by adding another compound that has the ability to stabilize the interface (Patel & Dewettinck, 2016). In the case of polymer gels, plasticizers are also used. In most cases, surfactants such as Tween 80 are used (Co & Marangoni, 2012). The viscoelastic properties of the polymer gels are dependent on the molecular weight, molecular structure, and quantity of the polymer (Davidovich-Pinhas, 2019).

4.2 | Factors influencing gelation

Gelling behavior of oleogelators is influenced by many factors such as type of gelator (chemical nature), type of sol-

vent (oil), gelator-solvent interaction, and the interactions between the microstructures at the junction zones (Doan et al., 2017; Martins et al., 2018; Trujillo-Ramírez et al., 2019). Oleogelation is greatly influenced by the type of gelator and type of solvent. The functional groups present in the gelators and their position promote interactions only in one direction (unidirectional) among gelator molecules and stereocentres (or chiral centers) have an effect on the molecular packing and subsequent association of molecular assemblies (Patel, 2017). The structure and polarity of the gelator determine the interactions among gelators (Co & Marangoni, 2012; Patel, 2017).

A gelator molecule must be rather insoluble in the oil to crystallize or self-assemble to create mesoscale structures. At the same time, the gelator should be comparatively soluble to interact with solvent molecules. That is, there should be an ideal balance between oil-gelator and gelator-gelator interactions to develop an oleogel (Co & Marangoni, 2012). The molecular characteristics of both gelator and oil determine these interactions. For example, the presence of functional moieties with hydrogen bonding sites and long alkyl chains in the gelator molecule and the polarity of the oil influence these interactions (Patel, 2018a). Therefore, due to the difference in the solvent-gelator interactions, oleogelators cannot function in the same way in all types of oils. For example, glycerol monostearate has been used as an efficient oleogelator at 25°C in high oleic sunflower oil, sunflower oil, and coconut oil. Nevertheless, the same oleogelator was unable to form a gel in flaxseed oil attributed to the higher unsaturation levels compared to other oils (Barroso et al., 2020; Ferro

et al., 2019). On the other hand, an ethylcellulose-based oleogel had improved mechanical properties when the oil is more unsaturated. That is, the flaxseed oil-based oleogel exhibited enhanced properties compared to canola oil and soybean oil (Laredo et al., 2011). These different behaviors of gelator–oil (solvent) interaction could be due to the differences in gelation behavior of gelators according to their composition and structure. Solvent properties influence the self-assembly pattern of gelators into their self-assembled fibrillar networks (Lan et al., 2015). A study on five different oil types with different degrees of unsaturation (rice bran oil, rape seed oil, corn oil, high oleic sunflower oil, and sunflower oil) reported that the minimum gelling concentration of the wax was significantly influenced by the fatty acid composition of the oil with the lower gelling concentrations required for the oil with less proportion of unsaturated fatty acid (Patel & Dewettinck, 2015). On the other hand, another study by Yilmaz et al. (2021) performed to develop oleogels from sunflower oil using five different types of waxes such as tea wax, rapeseed wax, orange peel wax, rose wax, and beery wax reported that the minimum gelator concentrations of these waxes ranged from 1.0% (sunflower wax) to 25% (rice bran wax), with gelation times of 0.3–205 min, respectively.

In the case of multicomponent gels, synergistic interactions among gelators also influence the process of self-assembly and self-organization. Microstructural changes in multicomponent gels are influenced by heterogeneous nucleation, nucleation rate, and crystal habit modification (Patel & Dewettinck, 2016). The firmness of the oleogels depends on the size of the crystals and the pore size. Finer crystals and the finer pore size enhance the oil entrapment of the network (Arjen Bot & Flöter, 2018). Therefore, the selection of a suitable oleogelator for a particular oil type should involve a broader view of different factors influencing their gelling behavior to get the required properties of the oleogels.

4.3 | Characterization of oleogels

Oleogel is a system consisting of liquid oil and gelator/s in a solid-like (semi-solid) state. The gelator/s form a network which embed the oil, and this network structure determines the properties of the resulting oleogel. The network consists of a complex hierarchical structure consisting continuous crystal growth from nanocrystals to microcrystals, and ultimately these crystals create a macro-level network structure (Valoppi et al., 2020). Therefore, to understand the mechanism of gel formation and to determine the properties of oleogels, it is necessary to character-

ize the structure of the oleogel from nano to macro level. Further, understanding the bonds at molecular level will further support the interpretation of characterization of oleogel from nano to macro level.

In brief, the characterization of oleogels includes the techniques for understanding the structure of the oleogel and the evaluation of their properties. The applicability of the oleogels in foods is determined using critical gelling concentration, solid fat content, texture, sensory properties, and spreadability (Puscas et al., 2021). Determination of critical gelling concentration of the structurant (minimum quantity of the gelator required to produce a nonleaking, nonflowing soft solid) is the very first consideration in preparing oleogels. The critical gelling concentration is determined by visual observation, usually by a tilt test (inverting the bottle containing the gel to see the gelation) (Flöter et al., 2021). For this purpose, oleogels are prepared using different concentrations of oleogelators (Barroso et al., 2020). This lowest concentration of the gelator depends primarily on the type of gelator and solvent (oil)–gelator interactions. Generally, a low amount of gelator is preferred due to economical as well as quality considerations. A very high amount of gelators may sometimes reduce the sensory quality of the resulting gel, for instance, waxes may create a waxy mouth feeling at higher levels (Shi et al., 2021). Another basic characteristic used in characterizing the oleogels (and usually for screening the gelator types and concentrations) is oil binding capacity (capability of the gel to entrap the oil). Oil binding capacity is the amount of oil that remains entrapped in the structure after providing external forces, usually centrifugal force (accelerated stability test) (Flöter et al., 2021). A new approach has been developed to determine the oil binding capacity by determining the weight increase of filter paper after keeping a block of oleogel on the filter paper (Omonov et al., 2010). However, the centrifugation approach is found to be the predominantly used method by many researchers. In the centrifugation approach, the oleogel is melted completely and added to the centrifugation tube, and stored (for 48 h) before applying the centrifugal force (4000–9000 rpm for 10–320 min). Following centrifugation, the released oil is drained by keeping the tubes inverted for about 30 min. The oil binding capacity is calculated based on the amount of oil held in the network after draining based on the weight differences. Even though the centrifugation approach is widely used by researchers, its accuracy is a concern (Flöter et al., 2021). Solid fat can be defined as the ratio of solid fat present in the oil at a specific temperature, and it influences the spreadability and organoleptic properties of the oleogel (Devi & Khatkar, 2016). The solid fat content of the oleogel is affected by the fatty acid composition, saturation level, and temperature (Guo, Cai, et al., 2020). Nuclear

magnetic resonance (NMR) is used to measure the solid fat content.

Macroscopically, hardness or texture and rheology measurements are used. These properties influence consumer acceptability. Hardness, a measure of gel strength or robustness, is one of the most vital attributes in influencing the food applications of the oleogel (Tavernier, Doan, et al., 2017). It is measured using a texture analyzer to get texture profile which gives information on firmness, adhesion, spreadability, chewability, and gumminess of the sample. Rheology is defined as the study of deformation and flow of matter in response to applied stress (Devi & Khatkar, 2016). The gelling points are determined by rheological measurements by subjecting the oleogel to a decreasing thermal treatment or isothermal treatment. Flow tests and oscillatory measurements like amplitude (strain and stress), frequency, temperature, and time sweeps can be performed using a rheometer. Oscillatory rheological measurements are used to classify the oleogels based on G' and G'' (which refer to solid-like and liquid-like behaviors, respectively) into strong gels ($G''/G' \leq 0.1$), weak gels ($0.1 < G''/G' < 1$), and viscous sols ($G''/G' \geq 1$) (Tavernier, Doan, et al., 2017). If the storage modulus (G') is higher than the loss modulus (G''), the oleogel displays a gel-like behavior. The microstructure and solid fat content of the oleogel determine the rheological parameters. The higher solid fat content of the oleogel results in higher rheological and textural parameters (Tavernier, Doan, et al., 2017). Rheological parameters may change during storage (Devi & Khatkar, 2016). Due to this reason, researchers evaluate the changes in rheological parameters during storage to determine the storage stability of the oleogels.

The primary structures on nanoscale and the molecular interactions (bonds) among the oleogelators and between the oleogelators and the oil can be examined by Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy. FTIR spectrum provides information on specific absorbances at the specific wavelength regions, whereas Raman shifts give details on the specific chemical bonds based on the changes in the shape and frequency of the bands corresponding to molecular vibrations (Puscas et al., 2021). For example, FTIR and Raman spectroscopy were used to find the intermolecular H bonding between the sitosterol and oryzanol in an organogel (Dalkas et al., 2018).

Crystal properties can be analyzed using X-ray diffraction (XRD) analysis. XRD analysis gives details on crystalline arrangement, crystal morphology, and size and molecular packing inside the crystals. Small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) are used to determine the morphology of the crystals. XRD analysis is one of the major characterization methods to determine the synergistic effects of oleogelators in multicomponent oleogels. Further, understanding

of polymorphic forms of the oleogels provides information on the stability of the oleogels. The crystals appear in α and γ forms, and upon heat treatment, they turn into β' (meta-stable) or β (stable) forms. The β' polymorphic shape mainly determines the textural and rheological parameters of oleogel (Puscas et al., 2021). NMR can be used to analyze the conformational changes at the molecular level during gelation using a magnetic field. This technique can also be used to determine the oxidative changes in the polyunsaturated fatty acids and to detect the primary and secondary products of oxidation (Alexandri et al., 2017). The use of techniques such as FTIR and Raman spectroscopy, XRD, and NMR to characterize the multicomponent oleogels will assist in getting knowledge related to the mechanism behind the oleogelation and synergism among gelators.

The microscopic characterization can be performed using different types of microscopes. The polarized light microscopy (PLM) and normal light microscopy enable the characterization at micrometric levels, whereas scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to investigate the structure and structural arrangements of the molecules at nanometric scales. Light microscopy is usually used as a complementary method for the SEM (Flöter et al., 2021). PLM gives details on crystal morphology, whereas SEM and AFM provide better visualization of the crystal network (Barroso et al., 2020). For example, the SEM was used to find out that the morphology of wax crystals is platelet like (Blake & Marangoni, 2015), which was earlier considered needle like (Blake et al., 2014).

The thermal properties such as onset and peak melting and crystallization points as well as the solid fat content of the oleogel can be performed using differential scanning calorimetry (DSC). The oleogel samples are subjected to heating and cooling cycles. The process of oleogelation involves heat treatments. Therefore, thermal analysis is important to analyze the process of oleogelation (Bhattacharya & Bhattacharya, 2014; Puscas et al., 2021).

4.4 | Synergistic effects of oleogelators

The use of combinations of oleogelators (binary and ternary systems) and the addition of a cogelator to get the oleogels with enhanced properties and to overcome the limitations of using a single oleogelator has been a focus recently (Patel, 2015). In most cases, the effective combinations have been discovered by happenstance (Barroso et al., 2020). Therefore, the understanding of the mechanism behind the synergism among gelators is crucial to explore the benefits of using combinations of

oleogelators to tune the properties of oleogels. Table 1 presents a summary of studies that used combinations of gelators to examine their synergistic effect on the properties of oleogel based on various edible oils.

The mixtures of sterols, most importantly, γ -oryzanol, and β -sitosterol have been extensively researched (Ashkar et al., 2019; Sawalha et al., 2012; Sawalha et al., 2011). Other combinations include fatty acids and fatty alcohols (Blach et al., 2016; Gravelle, Davidovich-Pinhas, et al., 2017), waxes and monoglycerides (Choi et al., 2020), and monoglycerides and phytosterols (Sintang et al., 2017). Moreover, synergistic interactions between oleogelators and additives such as surfactants (stearic acid with Span 60) (Uvanesh, Sagiri, Banerjee, et al., 2016) also have been demonstrated.

There are three groups of multicomponent gels based on the involvement of each component in gelation: (1) two or more components are needed to make gels where each component does not have the ability to form gels alone, (2) more than one compound is used where each compound can form gels, and (3) gelator(s) and nongelling additive(s) are used in mixtures to improve the gel properties. In the second category of multicomponent gel, which uses more than one gelator, the mechanism of gelation may be coassembling, where the gel (co-assembled gels) is formed due to the interaction between the gelators, or self-sorting, where the gel is formed by the assembled structures which are formed by each gelator individually. The combination of both coassembly and self-sorting is also possible (Pakseresht & Mazaheri Tehrani, 2020; Patel, 2017). Entanglement of the primary structures (coassembled or self-assembled or self-sorted fibers) with each other creates the three-dimensional network structure (Draper & Adams, 2018). Nongelling additives used in oleogels can function in different ways in modulating the crystal network of the oleogels such as modifying the pattern of self-assembly of gelators, improve the spatial arrangement of crystals, and strengthen the network interactions (Buerkle & Rowan, 2012). Generally, the combinations of gelators are considered to have an effect on the hydrogen bonding of polar functional groups, which in turn influence the self-assembling behavior (Sintang et al., 2017).

4.5 | Oleogels developed using two or more components where each component does not have the ability to form gels alone

Examples for the first category of multicomponent gels usually involve oleogels developed using surfactants. Surfactants are amphiphilic compounds having hydrophilic head and hydrophobic (alkyl) tail, and both these groups contribute to gelation. The hydrophilic groups form

hydrogen bonds and the hydrophobic tails form interaction with the oil. Even though a single surfactant cannot gel effectively, when a co-surfactant is added, that can form hydrogen bonds with available polar groups resulting in modifications in self-assembly patterns and stabilizing the network and preventing host aggregation by linking the host surfactant together via hydrogen bonding. These effects can alter the melting behavior (Sintang et al., 2017).

The most widely studied surfactant in oleogelation is lecithin. Lecithin is not an effective gelator when used alone (Bodennec et al., 2016; Sintang et al., 2017). However, it can change the microstructure of the oleogel by serving as a crystal habit modifier (Okuro et al., 2018). Modifications in crystallization such as self-assembly patterns induced by lecithin may result in a synergistic effect when used along with other compounds they cannot form gels on their own such as sucrose esters (Sintang et al., 2017), α -tocopherol (Nikiforidis & Scholten, 2014), and sorbitan tristearate (Pernetti, van Malssen, Kalnin, et al., 2007).

A study reported that the combination of sunflower lecithin and sorbitan tristearate can form gels in vegetable oil, although both of these compounds cannot form gel even at high concentrations (20% w/w). However, their mixtures with ratios between 40:60 and 60:40 (lecithin:sorbitan tristearate) were able to form a gel at 4% (w/w). Microscopy of the gels revealed needle-like crystals of approximately 10 μm in length. Lecithin modified the crystal habit of the sorbitan tristearate crystals. Lecithin also enhances the formation of weak junctions between the crystals, resulting in a network that can entrap the oil effectively in a firm gel (Pernetti, van Malssen, Kalnin, et al., 2007).

Sintang et al. (2017) demonstrated that sunflower lecithin modified the self-assembling behavior of sucrose esters in sunflower oil attributed to the decrease in the hydrophilic head-oil interactions. It was evidenced by the enhanced rheological properties and the new peaks that appeared in the small angle XRD. However, the authors did not study the molecular organization of the gel to understand the mechanism behind the synergistic effects between the two surfactants (Sintang et al., 2017). When lecithin and α -tocopherol are used in combination at the 1:1 ratio, coassembly of gelators formed cylindrical micellar structures stabilized through physical interactions. α -Tocopherol molecules are likely to modify the spatial organization of the molecules due to interactions between their hydrophilic groups and enhance the formation of cylindrical wormlike micelles (Nikiforidis & Scholten, 2014).

Few authors (Matheson et al., 2017a; Nikiforidis & Scholten, 2014) have reported that the addition of trace quantities of polar compounds like water (approximately 1% w/w) can modify the properties of oleogels favorably when lecithin is used as a cogelator. The addition of polar

TABLE 1 Summary of studies reported the synergistic interactions between oleogelators

Oil source	Oleogelator/s	Parameters used in the process	Major finding	Reference
Oleogels developed using direct method				
Oleogels developed using gelators where each gelator cannot form gel alone				
Sunflower oil	Lecithin and α -tocopherol	Lecithin and α -tocopherol were used at ratios of 1:0, 1:1, 1:2, 2:1, and 0:1 at 25% (w/w). Texture, SAXS, and microscopy (PLM) analyses were used.	α -Tocopherol did not form a gel at any concentration, but the mixture ratio of 1:1 produced gel. The firmness of the gel was increased with the addition of water (1.0% [w/w]). Coassembly of both compounds formed cylindrical micellar structures stabilized by physical interactions.	(Nikiforidis & Scholten, 2014)
Sunflower oil	Sucrose esters and lecithin	Sucrose esters and lecithin were used at ratios of 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, and 0:10 % (w/w). Rheology, microscopy (optical microscopy and cryo-SEM), DSC, and XRD analyses were used.	Lecithin induced the gelation of the at all studied ratios. The 7:3 combination was the optimum based on rheological properties	(Sintang et al., 2017)
Sunflower oil	Sorbitan tristearate and lecithin	Different lecithin:sorbitan tristearate ratios ranging from 0:100 to 100:0 (w/w) used at varying concentrations from 6, 8, and 12% (w/w). Microscopy, texture, XRD, rheology, and NMR analyses were used.	A synergetic effect was reported at the ratios of lecithin:sorbitan tristearate between 40:60 and 60:40, indicated by the firmness of the gel.	(Pernetti, van Malssen, Kalnin, et al., 2007)
Oleogels developed using gelators with gelling ability				
Sunflower oil	Behenyl alcohol and behenic acid	Different weight ratios between the behenyl alcohol and the behenic acid, 10:0, 8:2, 7:3, 5:5, 3:7, 2:8, and 0:10 were studied. Optical microscopy, DSC, SFC, SAXS, and WAXS analyses were used.	The ratios 8:2 and 7:3 (molecular ratio of nearly 3:1) produced oleogels with the highest hardness and stability. Morphology and size of the mixed crystals and their spatial distribution contributed to the synergistic effects.	(Callau et al., 2020)
Canola oil	Lauric acid and behenic acid	Mixtures of lauric acid and behenic acid (10:0, 8:2, 6:4, 5:5, 4:6, 2:8, and 0:10) were studied. DSC, XRD, microstructure (light microscopy), rheology, and oil binding capacity were used.	The ability of the mixture to form gel was directly related to the behenic acid concentration. The mechanical performance the mixture was impeded by the lauric leading to a softer gel compared to the simple addition of each component, suggesting an antagonistic effect between the two molecules.	(Harris et al., 2019)

(Continues)

TABLE 1 (Continued)

Oil source	Oleogelator/s	Parameters used in the process	Major finding	Reference
Soybean oil	Reinforced carnauba wax and adipic acid	Different mixtures of carnauba wax and adipic acid (6:0, 5:1, 4:2, 3:3, 2:4, 1:5, and 0:6) were used up to 6% (w/w). FTIR, XRD, DSC, and morphological analyses were used.	Enhanced thermal behavior, crystallinity, and oil binding capacity due to the new intramolecular or intermolecular hydrogen bonding formed due to the synergistic effects.	(Aliasl Khiabani et al., 2020)
Soybean oil	Beeswax, candelilla wax, and sunflower wax	Binary mixtures of beeswax, candelilla wax, and sunflower wax in pure form as well as in 5% wax oleogels were studied. DSC, SFC, microscopy (phase contrast light microscopy), and texture analyses were used.	Different ratios of candelilla wax with beeswax and sunflower wax with candelilla wax were found to be synergistic in terms of oleogel firmness. The firmest oleogels of all mixtures were made from 10:90 sunflower wax and candelilla wax. Sunflower wax dominated in crystallization of sunflower wax and beeswax mixture. Altered crystal size and crystal morphology contributed to synergism.	(Winkler-Moser et al., 2019)
Flaxseed oil	Berry wax and glycerol monostearate Sunflower wax and glycerol monostearate	Different ratios of both mixtures (100:0, 75:25, 50:50, 25:75, and 0:100) were studied. Rheology, DSC, microstructure (PLM, SEM), and oil binding capacity were investigated.	A positive interaction was found for sunflower wax and glycerol monostearate at the ratio of 1:1. The mixture of berry wax and glycerol monostearate oleogel showed a decrease in the dynamic moduli.	(Barroso et al., 2020)
Soybean oil	Monoglyceride (2-monoglyceride enriched with unsaturated fatty acid) and rice bran wax	2-Monoglyceride at 2, 4, or 6% (w/w) at 4% of rice bran wax was tested at concentrations of 1 g/100 g–10 g/100 g.	The combinations showed synergistic effects on gel properties. A mixture containing 6% of 2-monoglycerides and 4% rice bran wax produced oleogels with superior qualities than other ratios.	(Chen et al., 2021)
Soybean oil	Monopalmitate and carnauba wax	Monopalmitate and carnauba wax mixtures at different ratios (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, and 0:10) were evaluated. NMR, DSC, and oil binding capacity analyses were used.	The increase in carnauba wax content resulted in a W shape trend in oil binding capacity and eutectic effect in the solid fat content at 40, 50, and 60 °C. Based on the isothermal crystallization as characterized by Avrami equation, the mass ratio of 2:8 showed the synergistic effect.	(Shuaishuai Yang et al., 2020)

(Continues)

TABLE 1 (Continued)

Oil source	Oleogelator/s	Parameters used in the process	Major finding	Reference
Soybean oil, high-oleic sunflower oil	Candelilla wax, monoacylglycerols, and a fully hydrogenated oil (hard fat)	Mixtures containing different proportions of three gelators as designed by the central composite design were evaluated at the concentrations from 5 to 10% using the monocomponent gel made using candelilla wax as control. Microscopy (PLM), DSC, texture, and rheological analyses were used.	Incompatibility among gelators was observed. That is the incorporation of monoglyceride and hard fat to candelilla wax resulted in a softer gel than monocomponent gels, however, had improved rheological properties. A minimum of 3% of candelilla wax was needed to get a semisolid material independently of the amount of the other two molecules.	(da Silva et al., 2018)
Rapeseed oil	Monoglyceride and triacylglycerol	Mixtures of monoglycerides and high melting point triacylglycerols (0:6, 1:5, 2:4, 3:3, 4:2, 5:1, and 6:0) were evaluated for the effect on oleogels with and without high-intensity ultrasound. Rheology, texture, SFC, melting, optical microscopy, and XRD analyses were used.	The oleogel prepared using only monoglyceride showed the best physical properties, elasticity, and oil binding capacity and sonication negatively affected the properties at this ratio. The oleogels produced by mixtures of gelators showed poor properties indicating a possible antagonistic effect among them at the concentration evaluated (6%). However, sonication exerted a positive effect on the mixture of gelators.	(da Silva & Danthine, 2021)
Sunflower oil	β -Sitosterol and beeswax	Oleogels of β -sitosterol and beeswax were studied at varying ratios 0:10, 2:8, 4:6, 6:4, 8:2, and 10:0 (w/w) and used at 10, and 20% (w/w). DSC, texture analysis, FTIR, polarized light microscopy, and XRD analyses were used.	Oleogels made with beeswax as the only oleogelator had the highest hardness and maximum enthalpy change.	(Pang et al., 2020)
Sunflower oil	Monoglyceride and phytosterol	Combinations of monoglyceride and phytosterol (10:0, 8:2, 7:3, 6:4, and 0:10 (% [w/w]), DSC, rheology, microscopy (optical and cryo-SEM), and XRD analyses were used.	The ratio of 8:2 exhibited higher storage modulus (G') than the mono-component gels and contained a mixed crystal system. At this optimum ratio, the phytosterol synergistically improved the viscoelasticity of oleogel.	(Bin Sintang et al., 2017)
Sunflower oil	γ -Oryzanol and phytosterols	γ -Oryzanol:phytosterol mixtures at ratios, 30:70 and 60:40 (w/w) at the total concentration of 5, 10, 15, and 20% w/w were studied. Rheology, texture, and optical microscopy analyses were used.	Oleogel at the ratio of 30:70 produced stronger emulsion gels compared to the 60:40 ratio due to the interconnected aggregated crystallized (or partially crystallized) oil droplets.	(Moschakis et al., 2016)

(Continues)

TABLE 1 (Continued)

Oil source	Oleogelator/s	Parameters used in the process	Major finding	Reference
Sunflower oil	β -Sitosterol and stearic acid	β -Sitosterol and stearic acid were combined at (w/w) 1:0, 4:1, 3:2, 2:3, 1:4, and 0:1 and used at a concentration of 20%. The oleogel was analyzed using optical microscopy, FTIR, XRD, DSC, and texture.	The oil binding capacity, melting point, and firmness of the oleogel increased with the increase in the amount of stearic acid in the gelator mixture.	(Shu Yang et al., 2017)
Canola oil	Ethylcellulose and lauric acid	Combinations of ethylcellulose with lauric acid, at different ratios (0, 2, 4, 6, and 8% [w/w] ethylcellulose with 0, 3, 5, 8, and 10% [w/w] lauric acid, respectively) were analyzed. Texture, rheology, XRD, and DSC analyses were used.	The physical properties of oleogel was primarily influenced by ethylcellulose concentration. A transition from antagonistic to a synergistic effect between both components concerning the mechanical properties was observed above 4% (w/w) ethylcellulose.	(Eisa et al., 2020)
Canola oil	Stearyl alcohol:stearic acid and ethylcellulose	Stearyl alcohol:stearic acid at varying ratios (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, and 0:10, at 5% [w/w]) were studied in the presence of ethylcellulose (4%). Hardness, XRD, DSC, oil loss, SFC, and bright-field microscopy analyses were used.	Ethylcellulose modified the microstructure of the stearyl alcohol:stearic acid network. All ratios except 8:2 to 4:6 demonstrated a significant increase in gel strength in the presence of ethylcellulose, with the hardest composed of stearic acid only (0:10).	(Gravelle, Blach, et al., 2017)
Canola oil	Ethylcellulose and commercial monoglycerides	Oleogels were developed using two monoglycerides at 2 and 8% (w/w) in the presence of 6% ethylcellulose. Rheology, XRD, PLM, calorimetry, and oil binding capacity were used.	There was a synergistic interaction between monoglyceride and ethylcellulose that results in oleogels with higher viscoelastic properties and oil binding than those observed in oleogel developed using monoglyceride only.	(Lopez-Martinez et al., 2015)
Oleogels developed using gelator and nongelling additive(s)	Soy lecithin and ethylcellulose	The effect of different combinations of ethylcellulose and lecithin on the properties of oleogel was evaluated and compared with lard. SAXS, SEM, texture, and rheology analyses were used.	The addition of 1% (w/w) soy lecithin increased the shear moduli by 10-fold and gel hardness by 20-fold for 10% ethylcellulose oleogels, whereas a higher amount of lecithin caused a smaller increase.	(Aguilar-Zárate et al., 2019)
Sunflower oil	Soybean lecithin and fruit wax	Fruit wax and soybean lecithin were used at various ratios (100:0, 75:25, 50:50, 25:75, and 0:100). Rheology, DSC, microscopy (PLM and cryo-SEM), and Raman spectroscopy analyses were used.	A synergistic effect on the gel strength was observed at fruit wax:lecithin ratios of 75:25 and 50:50. Even below the critical gelling concentration of fruit wax, the addition of lecithin enabled gel formation.	(Okuro et al., 2018)

(Continues)

TABLE 1 (Continued)

Oil source	Oleogelator/s	Parameters used in the process	Major finding	Reference
Sunflower oil	Ceramide and lecithin	Lecithin and ceramide were used at various molar ratios (10:0, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 0:10). Microscopy (PLM), DSC, XRD, and FTIR analyses were used.	At two ratios (6:4 and 5:5), harder gels were formed with enhanced oil binding capacity (up to 99.84%) and displayed a higher tolerance level to permanent deformation than the monocomponent gel. Gelators coassembled at approximately equal molar ratio.	(Guo, Song, et al., 2020)
Soybean oil	Span 60 and stearic acid	Span 60 was mixed at 0, 1, 3, and 5% to the 19% of stearic acid in sunflower oil. Microscopy (bright field and confocal microscopy), DSC, XRD, and mechanical analyses were used.	Incorporation of Span 60 altered the crystallization kinetics, crystal habit, and crystal structure of stearic acid. Span 60 reduced the crystal size and modified the shape of stearic acid crystals from plate-like structure to a branched architecture.	(Uvanesh et al., 2016)
Oleogels developed using polymers as gelators using the indirect method				
Sunflower oil	Sodium caseinate, xanthan gum, and guar gum	Oleogel formulation was optimized based on sodium caseinate (0–4 g/100 g), xanthan gum (0–1 g/100 g), guar gum (0–1 g/100 g), and drying method (freeze and oven drier) using response surface methodology.	All responses were enhanced for the samples containing ternary mixtures of protein–gum as well as binary mixtures compared to samples containing protein or gums alone due to the synergistic effect of sodium caseinate and gums. The best formulation was the freeze-dried oleogel containing 4 g/100 g sodium caseinate, 0.43 g/100 g xanthan gum, and 0.98 g/100 g guar gum.	(Abdolmaleki et al., 2020)
Sunflower oil	Gelatin and xanthan gum	Different concentrations of xanthan gum with a constant amount of gelatin and different concentrations of gelatin with a constant amount of xanthan gum were evaluated. Microscopy (optical, confocal, and cryo-SEM), rheology, fracture studies, and droplet size and zeta potential were analyzed.	The mixture of gelatin and xanthan gum prevented the coalescence of oil droplets during drying of emulsion and strengthened the polymer layer of the oleogel. The change in xanthan gum concentration from 0.6 to 1.5% at a constant gelatin concentration (0.8%) did not have an influence on droplet distribution. However, the increase in the gelatin concentrations from 0.6 to 1.6% at a constant xanthan gum concentration (0.6%) reduced the size of droplets.	(Patel et al., 2015)

(Continues)

TABLE 1 (Continued)

Oil source	Oleogelator/s	Parameters used in the process	Major finding	Reference
Canola oil	Gelatin and xanthan gum	Gelatin and xanthan gum mixtures were used. Oil binding capacity, microscopy (optical, PLM, and SEM), rheology, storage stability, and FTIR analyses were used.	The use of a combination of gelatin and xanthan increased the firmness of the oleogel via physical interactions. Storage stability of the oleogel (in terms of oxidative stability) was also better than that of pure oil up to 2 months of storage. The mixture containing 3% gelatin and 0.2% xanthan produced the oleogel with the best quality among all combinations studied.	(Abdollahi et al., 2020)
Sunflower oil	Soy protein isolate and κ -carrageenan	Oleogels were prepared using soy protein isolate and κ -carrageenan at the ratio of 15:1 and soy protein only. Oleogels were analyzed by cryo-SEM and rheology.	Complexes formed at a ratio (15:1) improved the stability of emulsions compared to soy protein isolate. However, soy protein isolates produced stronger oleogels compared to the gel produced by the complexes.	(Tavernier, Patel, et al., 2017)
Camellia oil	Citrus pectin tea polyphenol–palmitate	Oleogels were prepared at a constant tea polyphenol–palmitate particles (2.5%) (m/v) and varying citrus pectin concentration of 1.5, 2.5, 3.5, and 4.5% (m/v). Rheology, oil loss, and oxidative stability were used.	With the increase in the citrus pectin concentration (>1.5%), the hardness, gel strength, and oil binding capacity of the gel were increased due to the interfacial accumulation of the tea polyphenol–palmitate particles and reduced coalescence by the thickened interfacial layer by the gel network formed by citrus pectin.	(Luo et al., 2019)
Sesame oil	Xanthan gum and egg white protein	Egg white protein (5%). Different concentrations of xanthan gum (0, 1, 0.5, and 0.75%) were used with egg white protein at 5% by using aerogels system. FTIR, XRD, SEM, texture, rheology, and oil binding capacity analyses were used.	Oleogel made using xanthan gum and egg white protein showed a highly porous and structurally stable matrix with high mechanical strength. An increase in the amount of xanthan gum increased the hardness of the gel.	(Jaberi et al., 2020)

solvents leads to micellar swelling and induces unidirectional growth of reverse micelles that transforms into polymer-like micelles (Sintang et al., 2017).

4.6 | Oleogels developed using two or more gelators where each gelator has the ability to form gel alone

In the second category of oleogels (coassembled and self-sorted gels), most of the studies reported that the major oleogelator is primarily responsible for creating the structured system such as crystalline particles or lamellar phases in the solvent where as the cogelator alters these basic structured systems into different structuring units that can create a space-filling crystal network (Patel, 2017). Examples for this type of gels include the use of combinations of fatty acids and fatty alcohols (Blach et al., 2016; Callau et al., 2020), sterols and sterol esters, and sterols and monoglycerides (self-sorting), and combinations of waxes from different sources (Winkler-Moser et al., 2019).

It is well established that the synergistic effects in these systems are due to the combined crystallization of finer crystals and altered crystal morphology. Fatty acids and fatty alcohols can gel alone when used in edible oils. Fatty alcohols with longer chain lengths (more than C18) are more efficient gelators compared to fatty alcohols with shorter chain lengths attributed to their differences in solubility and crystal sizes (Co & Marangoni, 2018). The use of combinations of both has gained much attention due to their synergistic effects. The use of combinations of fatty acid and fatty alcohol of the same chain length was reported by Gandolfo et al. (2004) for the first time, and this study has drawn the attention of other researchers to explore the synergism among fatty acids and fatty alcohols of the same chain length. They examined the fatty alcohols and fatty acids with the same chain lengths (C16–C22) on the texture of oleogels. The critical gelling concentration of the fatty acids, fatty alcohols, and their combinations was as low as 2% (w/w). At the concentration of 5% (w/w) in sunflower oil, the combination of fatty alcohols and fatty acids having the same carbon numbers demonstrated a synergistic effect at a temperature below 20°C at two specific ratios (7:3 and 3:7 (w/w) with the corresponding molecular ratios of 1:3 and 3:1). The enhanced microstructure was attributed to the influence of a larger number of small crystals on crystallization kinetics due to minimal interfacial tension at these two ratios (Gandolfo et al., 2004). Later, few other authors tried to understand further the mechanism behind the synergistic effects of the same system (Blach et al., 2016; Callau et al., 2020; Schaink et al., 2007). Schaink et al. (2007) studied the same system (stearyl alcohol:stearic acid), but

their results showed only one ratio (7:3) exerted the synergistic effect. The microscopy and XRD experiments of the system revealed that the enhanced effect is associated with mixed crystallization of fatty alcohol and fatty acid generating smaller platelet crystals compared to the pure components. Blach et al. (2016) also studied the same systems in canola oil and the optimum ratios of stearyl alcohol:stearic acid were 7:3 and 8:2 to produce oleogel with increased firmness and oil binding capacity. Following these studies, another group of researchers studied a similar system having behenyl alcohol and behenic acid (C22:0) in sunflower and soybean oils (Callau et al., 2020). Their findings were in accordance with Blach et al. (2016). The microstructure of all gels formed from these mixtures usually comprises platelet-like crystals; however, the size and appearance were influenced by the ratio. For the mixed crystals obtained by quasi-complete crystallization for the ratio of 8:2 and 7:3, higher crystalline content and morphology, size, and distribution of the crystalline material were well correlated with the better oleogel properties compared to other ratios. The total concentration of the structurant was kept constant at 10% (w/w). Both single component gels have large platelet-like crystals, and the length and the width of the crystals were on the order of magnitude of around 100–500 μm . The oleogels made from stearyl alcohol:stearic acid at the ratios of 8:2 and 7:3 had the highest hardness and the highest oil binding capacity and exhibited small platelet-like crystals with less than 50 μm in length and some needle-like structures (Figure 7). When the concentration of behenic acid increased (5:5, 2:8, and 3:7), the size of the crystals increased again (Callau et al., 2020). The mixed crystal system, that is the platelike crystals together with the needle-like crystals, also contributes to tuning the oleogel properties (Blach et al., 2016; Callau et al., 2020). Moreover, to the crystal size and morphology, the modeling approach based on the cellular-solid model of Gibson and Ashby (1997) demonstrated that the differences in oleogels properties were also linked to the spatial distribution of the crystalline mass inside the oleogel (Blach et al., 2016; Callau et al., 2020). All these findings reported similar results on the multicomponent system of using fatty acids and fatty alcohols of the same carbon number (same chain length); it can be concluded that oleogel properties were not only linked to the nature of crystals (pure stearyl alcohol, pure stearic acid, or mixed crystals) or their morphology but also on their spatial arrangement. However, since the nature of the oil also impacts the oleogel properties as shown by some authors (Gandolfo et al., 2004; Gravelle & Marangoni, 2018), it is necessary to examine the same combinations of oleogelators in different oils and their blends.

Few recent studies investigated the effect of the addition of ethylcellulose in a stearyl alcohol and stearic acid (7:3)

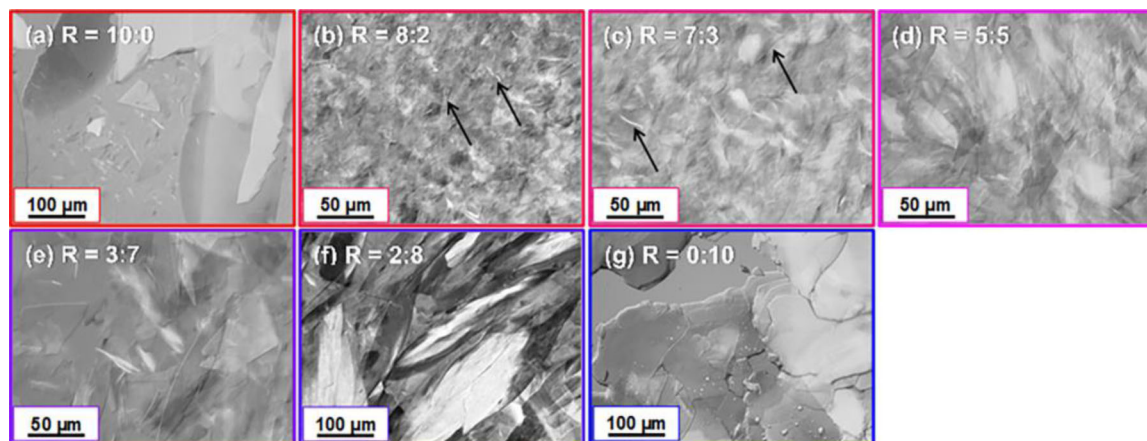


FIGURE 7 Differential interference contrast microscopy images of oleogels as a function of ratio (R) between behenyl alcohol:behenic acid in sunflower oil: 10:0 (a), 8:2 (b), 7:3 (c), 5:5 (d), 3:7 (e), 2:8 (f), 0:10 (g) (Callau et al., 2020)

oleogel (hybrid gel). The addition of ethylcellulose altered the crystallization of the oleogel resulting in increased plasticity of the resulting polymer network. Ethylcellulose modified the higher-order organization of the crystal network while maintaining the polymorphism of the mixed crystals of stearyl alcohol and stearic acid. Needle-like-oriented platelets were randomly distributed in the single component gels of stearyl alcohol and stearic acid, whereas the mixed component oleogels had branched, feather-like structures (Gravelle, Blach, et al., 2017; Gravelle, Davidovich-Pinhas, et al., 2017a, b).

The combinations of phytosterols and phytosterol esters are getting much focus as structurants for edible oils not only because of their gelling capacity but also because of their role in reducing blood cholesterol levels (Matheson et al., 2017b). γ -Oryzanol and β -sitosterol combination is the most extensively studied among others. They both can form gel alone; however, when they are used together, they can coassemble to form nanoscale tubular structures at certain proportions (Ashkar et al., 2019; Arjen Bot & Agterof, 2006; Bot et al., 2012; Martins et al., 2019; Matheson et al., 2017b; Patel, 2017; Sawalha et al., 2011, 2012). The hydrogen bond formed between the polar moiety of the phytosterol and the carbonyl group of oryzanol is considered to be responsible for the stacking of the molecules and the formation of a helical tubular structure (Scharfe & Flöter, 2020). Many researchers have studied the mechanism behind the formation of fibrillar tubules; however, they overlooked the mechanism of how these fibrils further assemble or aggregate. This was elaborated by Matheson et al. (2017b) using AFM. They have explained the hierarchical structure of this system. They demonstrated that the mixture of β -sitosterol and γ -oryzanol form the gel with complicated hierarchical structure formed by the self-assembly and aggregation of one-dimensional fibrils,

which aggregate into ribbons (not twisted strands). The thickness of the fibers are in the range of 30–400 nm (Matheson et al., 2017b). They also found the fibril diameters as \sim 9.8 nm, which agrees with the previously reported studies (8–10 nm) (Bot et al., 2012; Sawalha et al., 2012; Maria Scharfe et al., 2019). The previous studies have reported the ratio of 60:40 (γ -oryzanol:phytosterol) corresponding to the 1:1 mole ratio as the optimum to produce oleogels (Arjen Bot & Agterof, 2006; Martins et al., 2019; Matheson et al., 2017b; Perneti, van Malssen, Flöter, et al., 2007) (Figure 8). However, a later study (Moschakis et al., 2016) has reported that, at 30:70 ratio (γ -oryzanol:phytosterol), excess phytosterols crystallize to enhance the stability of the system, while the mixture at the ratio of 60:40 promotes fibril formation which improved gel strength. Higher firmness of gel at the ratio of 30:70 compared to the 60:40 ratio was attributed to the interlinked aggregated crystallized or partially crystallized oil droplets.

This combination has been studied for the structuring of different oils such as canola oil, sunflower oil, olive oil, flaxseed oil, rice bran oil, triolein, and castor oil (Sonia Calligaris et al., 2014; Moschakis et al., 2016). Gels formed from all oils showed a similar nanostructure; however, the type of oil had an impact on the gelling time and melting point of the oleogels. The melting characteristics of organogels based on flaxseed oil, sunflower oil, and extra virgin olive oil were similar at the same gelator concentration. In contrast, a noticeable reduction in the melting temperature of triolein and castor oil oleogels was observed attributed to the weaker gels. Regardless of the oil type, an increase in the hardness of oleogels was observed with the increasing concentration of the gelator. These findings indicate that the viscosity and polarity of the oil have an impact on the self-assembling behavior of the gelators. Oils with higher viscosity and polarity values result in oleogels with lower

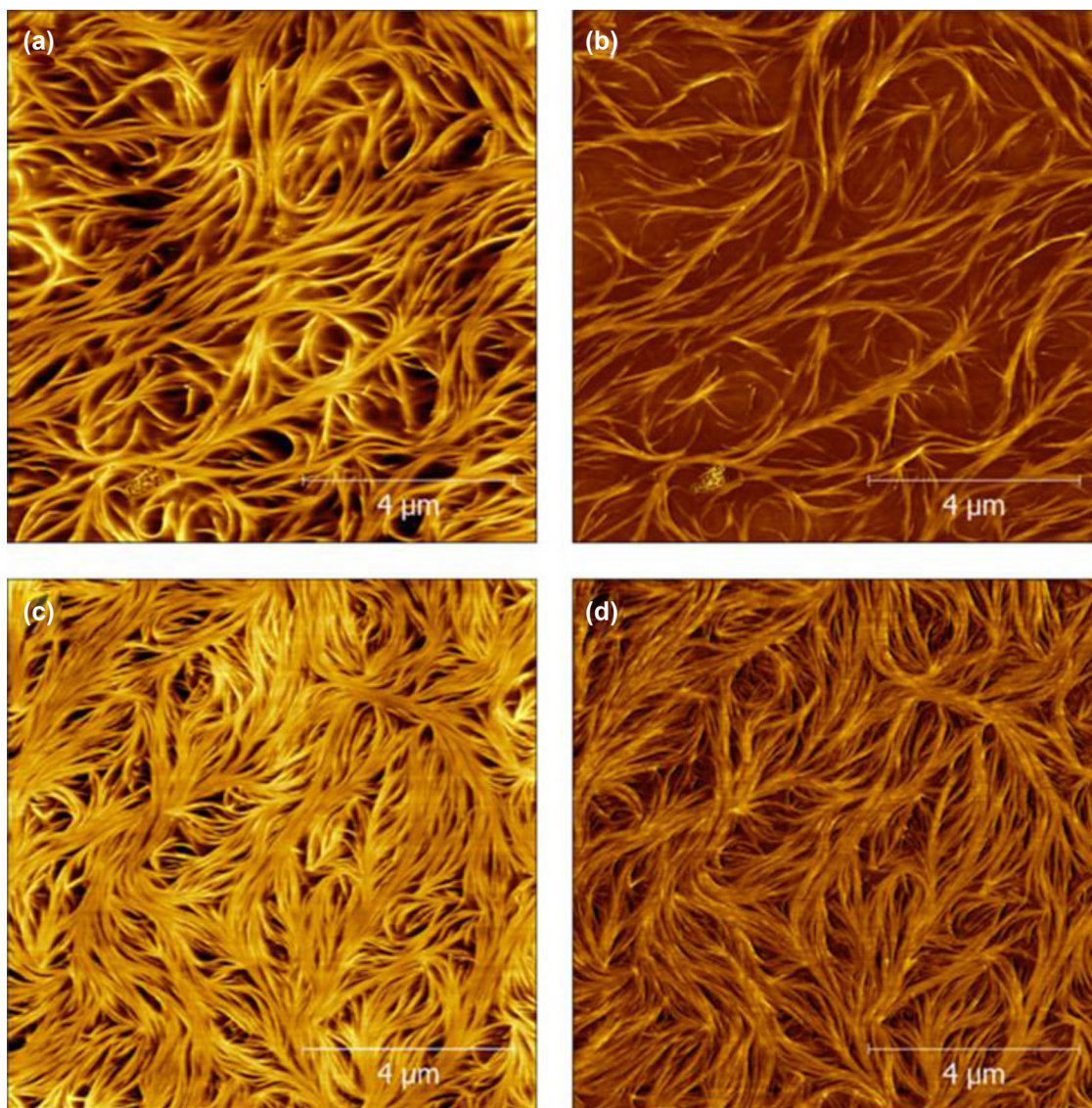


FIGURE 8 AFM height (left column) and phase (right column) images of 10% w/w (top) and 20% w/w (bottom) gels. Both samples show that fibrils aggregate into thick bundles (Matheson et al., 2017b)

firmness compared to those developed from oils with less viscosity and polarity (Sonia Calligaris et al., 2014). Among the oils examined, castor oil can form hydrogen bonds with gelators because of its high polarity due to the presence of ricinoleic acid which contains a hydroxyl group, resulting in the interference in gelator–gelator hydrogen bonds to form a network (Scholten, 2018). The results of these studies indicate the importance of giving attention to the type of oil as well in making oleogels.

The mixture of β -sitosterol and fatty acids also has been researched. Sun et al. (2021) showed that the β -sitosterol and stearic acid mixture (1:4, w/w) in corn oil produced a stronger gel with denser crystal network compared to the mixtures; β -sitosterol:oryzanol (2:3, w/w) and β -sitosterol:lecithin (4:1, w/w) (Sun et al., 2021). This study has selected the mixture ratios based on previous studies

(Han et al., 2014; Wendt et al., 2017; Yang et al., 2018). An increase in the amount of stearic acid in the β -sitosterol and stearic acid mixture resulted in enhancement in the oil binding capacity, firmness, and melting temperature in sunflower oil oleogel (Shu Yang et al., 2017). Both structurants showed self-sorting behavior in the oleogel, and the network was formed via physical entanglements stabilized by hydrogen bonding. Furthermore, XRD patterns of the oleogel prepared with the mixture indicated more predominant lateral packing of molecular layers compared with oleogel prepared with a single gelator. Further, an increase in the concentration of gelator mixture (3:2) from 10 to 30% (w/w) enhanced the oil binding capacity and firmness of the oleogel. The same research group (Shu Yang et al., 2018) further demonstrated that the oil type and concentration of gelators determine the melting and crystallization

behaviors of the oleogel. The group has evaluated the effect of oil type (corn oil, extra virgin olive oil, sunflower oil, and flaxseed oil) on the gelation mechanism of β -sitosterol and stearic acid at the ratio of 1:4. Gels developed from different oil types showed different microstructures, indicating the influence of oil type on the oleogel properties. Among the tested oils, and flaxseed oil oleogel exhibited highest firmness and oil binding capacity attributed to its lower viscosity of the oil compared to other oils. The viscosity of the oil depends on their unsaturated contents. Lower viscosity of the oil leads to higher firmness of the oleogel. Besides modifying the oleogels properties, the nature of the vegetable oil influences the optimum ratios of oleogelators (Callau et al., 2020) due to the differences in the interaction between the oil and gelators. Therefore, it should be noted that other ratios of the same mixture of oleogelator may produce oleogel with the enhanced properties of the oleogels prepared by the above-explained oil types. β -Sitosterol and beeswax combinations at different ratios in sunflower oil did not show any synergistic effect, and the monocomponent gel produced using the beeswax exhibited the highest strength and had a densely packed, spherical network, whereas the gel network formed by the sitosterol only had a needle-shaped network (Pang et al., 2020).

Lopez-Martínez et al. (2015) examined the effect of the addition of ethylcellulose to two monoglycerides (monopalmitate and monostearate) at 2% and 8% (w/w) in olive oil oleogels. Under static conditions, both monoglycerides formed weaker oleogels at 2%. Regardless of the concentration of both monoglycerides, the incorporation of ethylcellulose at a concentration (6%) below its critical gelling concentration resulted in increased viscoelastic properties and reduced oil loss during 14 days of storage at 15°C, especially for the oleogel with glycerol monostearate at 8%. These enhanced effects were attributed to the addition of ethylcellulose which lowered the rate of polymorphic transition of sub- α to β form and the following agglomeration of β crystals due to the limited molecular mobility (Lopez-Martínez et al., 2015).

The synergistic effects of phytosterols and monoglycerides also have been reported (Bin Sintang et al., 2017). They demonstrated the synergistic effect among gelators via the higher elastic modulus of the mixed component oleogel compared to their monocomponent gels. Even though both can form gels with liquid oils alone, these monocomponent oleogels have less stability upon storage compared to the mixed component gel formed by the mixture of phytosterol and monoglyceride. The oleogel developed with phytosterol only showed agglomeration of crystals leading to shrinkage of crystalline phase and subsequent syneresis of the oil from the system. Oleogels prepared with monoglycerides showed a polymorphic transition to form β -crystals during storage, which gives a gritty

texture to the oleogel. However, the combination of both at the optimum ratio of 8:2 (monoglyceride:phytosterol) (10% [w/w]) resulted in enhanced crystallization in the resulting oleogel. Microscopic images of the mixed component gel revealed the formation of self-sorted crystals and the phytosterol reduced the large agglomeration of monoglyceride crystals and reduced the crystalline aggregates (spherulites) (which is a drawback in monocomponent gels) of monoglyceride crystals resulting in an enhanced spatial arrangement of the crystals. The self-sorted fibers and spherulitic crystals resulted in a synergistic effect to enhance the properties of the gel.

Using the mixture of wax and monoglycerides has been studied by few researchers (Barroso et al., 2020; Chen et al., 2021; Choi et al., 2020; Shuaishuai Yang et al., 2020). Barroso et al. (2020) evaluated the combination of berry wax (low melting wax) or sunflower wax (high melting wax) with glycerol monostearate to determine the combined effect on the gelation of flaxseed oil. They reported that berry wax:glycerol monostearate combination showed a negative effect on dynamic moduli, and oil holding capacity of the oleogel attributed to the hindrance of the complete organization of berry wax in polyunsaturated chains of the oil by glycerol monostearate. In contrast, the mixture of sunflower wax and glycerol monostearate exhibited a positive interaction where both alone were not able to form the structure in flaxseed oil. It is because of the interaction between the polar heads of glycerol monostearate and the polar parts of fatty alcohols of the sunflower wax. The berry wax has less amount of fatty alcohols with polar groups compared to sunflower wax. Choi et al. (2020) reported that the mixture of candelilla wax with glyceryl monostearate at the ratio of 75:25 in grapeseed oil oleogels with improved texture and viscoelasticity, and with reduced syneresis attributed to its fine crystals arranged densely in a structural network as shown by the phase-contrast microscopic images. Similarly, Yang et al. (2020) also reported the synergistic effect of mixtures of monopalmitate and carnauba wax in soybean oil oleogel. The increase in carnauba wax content resulted in a W shape trend in oil binding capacity and eutectic effect in the solid fat content at 40, 50, and 60°C. Based on the isothermal crystallization as characterized by Avrami equation, the mass ratio of 2:8 showed the synergistic effect. Chen et al. (2021) also studied the mixture of monoglyceride and rice bran wax on soybean oleogels; however, they have given a focus on evaluating the effect of enriched 2-monoglyceride (containing about 93% of unsaturated fatty acids produced by enzymatic synthesis). The reason for choosing 2-monoglyceride with unsaturated fatty acid at the *sn*-2 position was its beneficial effect of reducing the fat accumulation in the body. They demonstrated the synergistic effects on gel properties in all combinations

studied, however, with the optimum when using the mixture of 4% rice bran wax and 6% 2-monoglycerides. Even though the authors did not report the results comparing with the commercial monoglycerides which contain mainly fatty acids at the *sn*-1 position, the effect of the position of the fatty acid at the monoglyceride cannot be determined from these results. However, this study has proposed a strategy to enhance the nutritional quality of the multicomponent gels while reporting the synergistic effects between the gelators. Studies reporting these types of techniques considering enhancing the nutritional value of the oleogels at the same time exploring the synergism among gelators are limited in the literature.

A study was reported to evaluate the gelation of binary and ternary mixtures of monoglyceride, candelilla wax, and hard fat (partially hydrogenated fats) on two types of oils such as soybean and high-oleic sunflower oils (da Silva et al., 2018). The incorporation of monoglyceride and hard fat to candelilla wax resulted in weaker gels, however, with improved rheological properties. Further, they reported that the effect on gel properties primarily depends on the proportions of gelators, but not on the total concentration of the gelator mixture. The soft gels produced by the mixtures could be attributed to the less interactions among gelators as evidenced by the microscopy images. A similar observation was reported in a later study on the combination of monoglyceride and wax (da Silva & Danthine, 2021). This combination has been studied in order to enhance the synergistic effects among monoglyceride and wax using high-intensity ultrasound. Though the ultrasound showed a positive effect on the properties of oleogels produced by the mixtures, the gels produced using the combination of both gelators without the application of high-intensity ultrasound produced a softer gel than the monocomponent gels produced using monoglyceride only which indicate a possible antagonism among the two gelators at the specific ratios studied. The reason for the poor interaction could be the independent crystallization of the gelators. However, an in-depth analysis of the mechanism behind the incompatibility among these gelators using XRD or other techniques to study the crystal structures and crystal organization is needed.

Different combinations of waxes have been researched for their potential synergistic effects. Researchers have demonstrated that when two waxes with different compositions are used in oleogels, they show a tendency to create eutectic or monotectic systems with small size crystals densely packed in the system (Tavernier, Doan, et al., 2017a; Winkler-Moser et al., 2019). Some combinations have been shown to exhibit synergistic effects, whereas some combinations are demonstrated to have negative effects when used together. For instance, Winkler-Moser et al. (2019) studied the

binary mixtures of candelilla wax, beeswax, and sunflower wax in sunflower oil oleogels. Some combinations of candelilla wax with beeswax and candelilla wax with sunflower wax exhibited synergistic effects on oleogel firmness. It is understood from the images of phase-contrast light microscopy that the enhancement of gel strength was associated with platelets with smaller dimensions and the interaction between spherulites and platelets. On the other hand, other ratios of the same combinations were reported to negatively influence the oleogel formation resulting in oleogel with reduced firmness. The combination of reinforced carnauba wax and adipic acid (a linear dicarboxylic acid) in sunflower oil oleogels resulted in enhanced thermal behavior, crystallinity, and oil binding capacity due to the new intramolecular or intermolecular hydrogen bonding formed due to the synergistic effects among them. Adipic acid acts as to enhance nucleation and crystallization due to cross-linker potential (Aliasl Khiabani et al., 2020).

In contrast to the combinations reported above, which showed synergistic effect at specific ratios of the combination of the gelators, a recent study on using mixtures of lauric acid and behenic acid (10:0, 8:2, 6:4, 5:5, 4:6, 2:8, and 0:10) demonstrated the antagonistic effect at the studied ratios. The mechanical performance of the mixture was impeded by the lauric acid leading to a weaker gel compared to the monocomponent gels of both compounds, indicating an antagonism between these two compounds. A comparable effect was seen for different concentrations of total structuring agents (10, 15, 20, and 30%) (Harris et al., 2019). The reason behind the negative or the positive (synergistic) interaction could be based on the solubility properties of the oleogelators. The solubility characteristics of oil and the gelator should have a balance to form a gel (Gravelle et al., 2016). When the oil and the gelators have different solubility balances, they will have different effects on the properties of oleogels (Okuro et al., 2018).

4.7 | Oleogels developed using gelator that can form gel alone and nongelling additive(s)

Nongelling additives can enhance changes in the crystallization kinetics, modify crystal habit, and stabilize the gel by preventing aggregation and contraction of crystals during storage. The modifications in the crystallization kinetics and crystal habits could enhance the thermal and mechanical properties of the gel (Patel, 2017, 2018a). Under the third category of multicomponent gels, lecithin is found to be an extensively studied nongelling additive together with another effective gelator. The mechanism behind the interaction of lecithin with other gelators was explained as the hydrogen bonding between the head

group of the lecithin (phosphate) and the polar moiety of another gelator (Matheson et al., 2017a). In addition to lecithin, Span 60 (Uvanesh, Sagiri, Senthilguru, et al., 2016) and Tween 20 (Uvanesh, Sagiri, Banerjee, et al., 2016) also have been reported in making oleogels.

In a study investigating the effect of lecithin with fruit wax in gelation of sunflower oil, a synergistic effect was demonstrated between fruit wax:lecithin at ratios of 75:25 and 50:50 on the gel strength compared to the oleogels made by corresponding single components. The lecithin with wax reduced the onset of crystallization temperature. Moreover, the addition of lecithin enabled gel formation even below the critical gelling concentration of fruit wax (Okuro et al., 2018). The advantage of using waxes with another molecule having a synergistic effect is that the reduced amount of wax due to the synergistic effect helps reduce the waxy mouthfeel without negatively affecting the oleogel characteristics. However, lecithin does not act as a crystal habit modifier in all cases. For example, Okuro et al. (2018) demonstrated that the presence of lecithin reduced the gelation capacity of the high melting point waxes such as beeswax, carnauba wax, candelilla wax, and sunflower wax in sunflower oil, whereas the combination of lecithin and low-melting (fruit wax and berry wax) waxes forms gels (Okuro et al., 2018).

A synergistic effect between lecithin and stearic acid in canola oil oleogel was reported. The primary structure of the oleogel contained the fibers formed by clustering of wormlike reverse micelles, which overlap to form a network that interacts with stearic acid crystals which appeared as aggregated thin fibers with continuous branching. The synergistic effect of the gelators (particularly at the ratio of 7:3) was indicated by the harder texture of oleogels based on a combination of both gelators compared to that of oleogels based on single oleogelators (Gaudino et al., 2019). A study performed to evaluate the gelation mechanism of the combination of lecithin (noneffective gelator) and ceramide (effective gelator) in sunflower oil reported an interesting finding that stable gels with superior oil binding capacity can be formed with a mixture containing a higher amount of lecithin than ceramide, whereas the mixture containing more amount of ceramide than lecithin resulted in poor gelation. The coassembled fibers of both compounds and the self-sorted crystals aggregated on the microscale by lateral association. Van der Waals forces and hydrogen bonding were present between the phosphate group of the lecithin and the amide group of the ceramide (Guo, Song, et al., 2020).

Aguilar-Zárate et al. (2019) have demonstrated that soy lecithin alters the rheology of ethylcellulose oleogels. They reported that the addition of 1% (w/w) soy lecithin to 10% ethylcellulose (w/w) increased the shear moduli by 10 times and hardness 20 times for oleogels. Increased

levels of lecithin as well as the increased level of ethylcellulose resulted only in a small increase in the above values. All oleogels were thermoreversible; nevertheless, gels containing lecithin exhibited an extra peak at high temperatures (120–130°C), indicating the existence of additional self-assembled structures (Aguilar-Zárate et al., 2019). The authors did not explain the mechanism involved in the molecular interactions between ethylcellulose and lecithin.

Han et al. (2014) analyzed the impact of using a mixture of lecithin and β -sitosterol on the properties of oleogel. The mixture at the proportion of 8:2 (β -sitosterol:lecithin) resulted in the harder gel than the monocomponent gels. The addition of lecithin changed the morphology of the β -sitosterol crystals from a rosette-like to a fibrillar structure (Han et al., 2014).

The role of surfactants (sorbitan monostearate, sorbitan monooleate, glycerol monostearate, and glycerol monooleate) in plasticizing the ethylcellulose-based oleogels have been studied (Davidovich-Pinhas et al., 2015b). The addition of surfactants increased the mechanical strength, and the authors have interpreted that the effect could be due to the self-assembly of surfactants due to their amphiphilic nature. However, the authors did not explain the mechanism of how these surfactants interact with the ethylcellulose network and their role in enhancing the strength of the gel. Incorporation of Span 60 and Tween 20 to stearic acid-based oleogels was examined. Both surfactants altered the crystallization kinetics, crystal structure, and crystal habit of stearic acid; however, the way of modification was different for both surfactants. Span 60 enhanced the formation of fine crystals of stearic acid and modified the shape from plate like to a branched architecture resulting in a positive effect on oleogel properties. On the other hand, the addition of Tween 20 to the stearic acid exerted a negative effect on oleogel properties because Tween 20 increased the ordered arrangement of stearic acid crystals leading to reductions in thermal stability and firmness (Uvanesh, Sagiri, Senthilguru, et al., 2016). The highly ordered arrangement of crystals reduces the imperfections in the structure and leads to large size pores. These pores will promote the syneresis of oil.

4.8 | Oleogels developed using other polymer gelators

Compared to the volume of research carried out on using low molecular weight oleogelators to make oleogels, the studies on using polymers (except ethylcellulose) as oleogelators are limited. Different polysaccharides such as starch, pectin, xanthan gum, and guar gum are

being used as thickeners, stabilizers, and gelling agents in various food applications. The use of proteins and protein–polysaccharide complexes as stabilizing agents in food emulsions is widely practiced. A nonsurface-active polysaccharide and a surface-active protein are added to an emulsion, the polysaccharide can enhance the protein network strength, and helps to structure the bulk oil phase leading to a stabilized system. Proteins and polysaccharides interact with each other via H bonds between –NH and –OH groups and hydrophobic interactions (Patel et al., 2015). Few authors have reported the effect of gelator mixture consisting of proteins and polysaccharides on the oleogel properties.

Patel et al. (2015) studied the combination of gelatin (protein) and xanthan gum (polysaccharide) on the properties of sunflower oil oleogel using the emulsion-templated method. This combination modified the emulsion properties into thicker emulsion compared to the emulsion stabilized only by gelatin that showed a fluid nature. Generally, the oil-in-water emulsions stabilized by either polysaccharide or protein shows the separation of phases during drying due to coalescence. However, when the emulsion is stabilized by the mixture of gelatin and xanthan gum, phase separation did not occur during drying. The microstructure oleogels had the oil droplets firmly packed together in a layered network of polymers, which inhibit the coalescence of oil droplets (Patel et al., 2015). The same combination of gelators (gelatin and xanthan gum) has been studied by Abdollahi et al. (2020) for the preparation of oleogels based on canola oil using a foam-templated approach. The oil binding capacity of oleogels was >92% which was less compared to that reported by Patel et al. (2015) (>97%) who used the same mixture using the emulsion-templated method. This difference in the oil binding capacity could be due to the oil type or processing conditions. Anyhow, both studies have demonstrated a positive effect of using the combination of gelatin and xanthan gum to make oleogel with enhanced mechanical properties. Further, Abdollahi et al. (2020) demonstrated that the gelatin and xanthan gum network resulted in the oleogel with better storage stability (in terms of oxidative stability) compared to pure oil up to 2 months of storage.

Similarly, another study was reported on using unmodified proteins (soy protein isolate) and protein:polysaccharide (κ -carrageenan) complexes (at the ratio of 15:1) to prepare oleogels. Rheological studies, protein load measurements, and cryo-SEM imaging showed that the enhanced stability of emulsion prepared using the complex was due to interfacial accumulation of the complexes rather than the increase in the bulk viscosity. However, the unmodified proteins produced stronger gels compared to the complex attributed to the suboptimal interfacial conformation of the soy protein

when fixed in a complex with κ -carrageenan (Tavernier, Patel, et al., 2017b). Egg white protein and xanthan gum combination has also resulted in oleogel with improved network structure with good mechanical strength (Jaberi et al., 2020).

Luo et al. (2019) reported the preparation of oleogels using citrus pectin and tea polyphenol–palmitate by the emulsion-templated method. They evaluated the pectin concentration of 1.5, 2.5, 3.5, and 4.5% (mass by volume) with a constant tea polyphenol–palmitate (2.5% mass by volume). The emulsion formed only by tea polyphenol–palmitate particles did not form a gel rather resulted in phase separation of oil upon freeze drying. However, the incorporation of pectin lead to gel formation, and the increase in the amount of pectin strengthened the network and the oil binding capacity. Though the authors reported a synergism among the gelators, they have not identified the interaction among gelators to elucidate the mechanism behind this effect. Optimization of parameters of oleogel manufacture using sodium caseinate, xanthan gum, and guar gum (binary and ternary mixtures) reported the synergistic effects among gum and sodium caseinate and gum leading to strong gel (Abdolmaleki et al., 2020). The authors did not analyze the microstructure of the oleogel. Therefore, the mechanism behind this synergism cannot be interpreted.

Recently, few authors tried to combine the indirect approach and direct approach of oleogelation to enhance the properties of oleogel. Since waxes have good gelation properties, authors attempted to use wax with polymers such as starch (Gao & Wu, 2019; Tavernier et al., 2018). Tavernier et al. (2018) reported that gel strength was not influenced by the addition of waxes in the emulsion-templated oleogels; however, wax incorporation had a strong influence on reducing the shear sensitivity of the oleogels. Similarly, the influence of the addition of monoglyceride and wax (candelilla) on protein (pea and fava bean proteins) foam-templated oleogelation of canola oil was studied. The addition of monoglyceride and wax enhanced the properties such as oil binding capacity, firmness, cohesiveness, and storage moduli of the oleogels (Mohanani et al., 2020). This new aspect of oleogelation could be explored further.

5 | CONCLUSIONS

Oleogelation has been considered as a promising alternative technique for the traditional oil structuring technique to produce structured fats with no *trans* fats and reduced saturated fatty acids. A plethora of research has been done using different gelator–oil systems during the past decade. Despite the oleogels having shown a great deal of promise, there are no oleogels used commercially for food

applications so far. The major challenge in the application of oleogels in food products is their deficiencies in monocomponent gels to mimic the functionalities, especially, the mouthfeel and texture of traditionally used fats. In recent years, the use of combinations of oleogelators to make oleogels has received considerable critical attention from researchers. There is an enormous number of publications reporting the synergistic effect of different combinations of oleogelators which contribute to tuning the properties of oleogels and overcoming the issues related to the monocomponent gels and will be a turning point to make the industrial applications of oleogel in foods a reality. Even though considerable literature has grown up recently around the theme of synergism among oleogelators, there are distinct knowledge gaps in this field that need to be addressed by scientists.

6 | FUTURE PERSPECTIVES

The primary challenge in developing oleogel with all desired properties is attaining the required microstructure which influences the macro-properties of the oleogels. As already discussed in this review, multicomponent oleogels offer many advantages to overcome the bottlenecks associated with the monocomponent gels. Understanding the mechanism behind the multicomponent gel/synergistic effects among oleogelators is pivotal to facilitating the further exploration of oleogelation to connect the science with the practical application. A plethora of research papers demonstrating the synergistic effects among oleogelators have been published. Below is a brief of possible mechanisms of synergism among gelators that can be understood from the published works.

The mechanisms could be summarized as follows; modification in the crystallization (self-sorting or cocrystallization), crystal size and morphology, and arrangements of crystals (spatial distribution). When two components (two gelators each of which can form gel alone or one gelator + nongelling additive or two gelators that cannot form gel alone) are used together to make gels, synergistic effects could be attained at particular proportions of the compounds. The mechanism behind the synergistic effect is dependent on the type of components used to make gels. When two gelators are used, they may enable the formation of finer crystals and alter the crystal morphology due to co-crystallization and enhance the spatial distribution of the mas. However, the oleogelators which have large differences in molecular structure do not co-crystallize; instead, they are self-sorted independently of each other to create a characteristic crystal network. This type of self-sorted crystal network improves the spatial distribution of crystals and thus, can prevent aggregation of the crystal, which is a

major limitation in monocomponent gels. For instance, the mixture of phytosterols and monoglyceride exhibited synergistic effects at particular proportions with a self-sorted crystal structure. The crystals of phytosterols can prevent the formation of large crystalline clusters of monoglyceride (Sintang et al., 2017). The synergistic effects of gelators and surfactants (nongelling additive) such as lecithin occur due to the influence of surfactant on the morphology and aggregation pattern of the crystals and reinforcement of network junctions among the crystalline units. The finer and strengthened network can physically entrap the liquid oil and enhance other mechanical properties. Further, the additive contributes to the stabilization of the gel by conquering postcrystallization events and improving the properties of the gel (Patel, 2018a). When two compounds that cannot form gel alone on their own are used to make the gel, both compounds get connected to the structure by weak junctions to form needle or plate shape crystals. For example, Perneti, van Malssen, Kalnin, et al. (2007) reported a synergistic effect between lecithin and sorbitan tristearate, both of which cannot form gel on their own.

The use of new characterization methods would contribute to a more comprehensive knowledge base for the successful development of oleogels. Understanding the crystal structure such as primary structures in angstrom to nanometer scale and bonds between the atoms in nanometric scale would help in this regard. This can be accomplished by using the techniques such as XRD, FTIR, Raman spectroscopy, small angle neutron scattering (SANS), and small angle X-ray scattering (SAXS).

Moreover, many of the researchers gave poor attention to evaluating process parameters on oleogel properties and storage stability. Lipid oxidation is the primary deteriorative process occurring in lipids that affect not only the nutritional qualities but also the sensory and textural properties. In addition to the oxidative and associated changes, the postcrystallization processes such as aggregation and contraction also got little consideration by many researchers. Another key point that this review identified is that research focus should be given on the nature of the oil because few authors have demonstrated that the same gelator mixture could behave differently in different oil due to the differences in the balance between solvent-gelator and gelator-gelator interactions. Despite the role played by the nature of oil in oleogel properties, only little effort has been made on this aspect. Since these interactions depend primarily on the polarity, chain length, positional distribution of fatty acids in the glycerol molecule, and packing of the chain length the studies can be designed to study the synergistic effects of oleogelators on modified lipids such as oil blends, interesterified lipids or fractionated oils. In addition to attaining the desired microstructure, this focus on using modified lipids could

be used as a means of improving the nutritional value of the oleogels by modifying the fatty acid composition of the oil and positional distribution of the fatty acids, because most edible oils in their natural form do not possess the ideal fatty acid composition needed for the good health. There are some types of oleogelators with much potential to be used economically to tailor the properties of oleogels and provided only a little attention. For instance, the monoglycerides are available commercially as food additives and have been studied by many researchers. Even though the commercial monoglycerides are usually complex mixtures, none of the authors reported the exact composition of the monoglycerides they have used to make oleogels, and none of the studies have evaluated the possible synergistic effects or the interaction of the constituents of the commercial monoglycerides on the oleogel properties. Therefore, future studies directed towards these types of oleogelators which got only a little attention could benefit the field of oleogelation. Further, future research should focus more on the applications of oleogels in different food products and sensorial analysis and incorporation of bioactive compounds, and their bioavailability to ensure healthier oleogels compared to traditional ones.

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AUTHOR CONTRIBUTIONS

Subajiny Sivakanthan : Conceptualization-Lead, Investigation-Lead, Writing – original draft-Lead, Writing – review & editing-Equal Terrence Madhujith: Conceptualization-Supporting, Project administration-Supporting, Supervision-Supporting, Writing – review & editing-Supporting Sabrina Fawzia: Conceptualization-Supporting, Project administration-Supporting, Supervision-Supporting, Writing – review & editing-Supporting Azharul Karim: Conceptualization-Supporting, Project administration-Lead, Supervision-Lead, Writing – review & editing-Supporting

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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