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Alternative Routes to Oil Structuring

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Preface

> Ooh what about gels? This is embarrassing to admit, but I haven't even thought about gels.
>
> (The Simpsons, Covercraft 2014)

In the last few years, oleogels and oleogelation have transformed from relatively unheard terms to a well-explored research domain in food lipid science. The sudden rise in the interest in this area is clearly indicated from a rapid increase in the number of oleogel-related publications appearing in both field-specific (food and lipid science journals) and multi-disciplinary journals. At least from a basic research perspective, oleogelation has been hailed as a promising oil structuring strategy that can help us formulate food products with significantly lowered levels of saturated fats. Besides the industrial need for such an approach, the main driver for such increased interest in this area has to do with the interesting properties of oleogel systems that make them an attractive subject for fundamental and explorative research.

Considering the enormous potential of oleogels, it is currently regarded as a 'hot-topic' among food researchers and if the current trend is anything to go by, more concrete applications of oleogels in commercial food systems are expected in the near future.

The purpose of this *Springer Brief* is to give an overview of some recent research in the area of oleogelation with the main focus of providing practical guidelines for new researchers starting their work in this area. Chapter 1 gives a concise but comprehensive overview on different categories of structuring agents that have been researched so far, followed by chapters where structurants such as natural waxes, hydrophilic food polymers, and colloidal particles are discussed individually, to have a detailed understanding about characterization of oleogels. Potential food applications of oleogels covered in Chap. 5 should be of particular interest to industrial scientists working in the area of healthy structuring of foods. This book ends with a discussion on general considerations in terms of advantages and drawbacks of some of the most promising and researched oleogel systems.

It is an honest attempt of the author to provide a succinct account on edible oleogels from a practical point of view such that new researchers starting their work in the area of oil structuring can use this information as general guidelines. I believe this *Springer Brief* will be of interest to both academic and industrial scientists working in the area of lipid science and technology.

Gent, Belgium Ashok R. Patel

Acknowledgement

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Contents

Chapter 1
Introduction

Abstract The conventional approach for structuring oil that is currently used in the food manufacturing industries relies heavily on the use of crystalline triacylglycerols (TAGs) as the building blocks. Since these high melting TAGs are rich in trans- and/or saturated fatty acids, the nutritional profile of such structured oil systems is unhealthy and from a processing point, structuring with this approach requires higher crystalline mass fraction (≥ 0.2 or 20 %wt). Alternative approaches that are based on the use of non-TAG building blocks as structurants could be explored to achieve efficient structuring at comparatively lower concentrations. This chapter gives an overview of different building blocks such as crystalline particles, self-assembled structures, polymeric strands, emulsion droplets, and colloidal inorganic particles that can be used for creating oleogels.

Keywords Oil structuring · Oleogels · Building blocks · Food polymers · Natural waxes · SAFiNs

1.1 Fat Crystallization—a Conventional Route to Oil Structuring

Oils and fats are chemically defined as triacylglycerols (TAGs) that are liquid and solid respectively at room temperature. The physical state that differentiates these two types of lipids is caused by the presence of a high proportion of high-melting or crystalline TAGs in solid fats. A triacylglycerol molecule is made of a glycerol backbone and three fatty acid (monocarboxylic acid) chains which are esterified to the hydroxyl groups of glycerol. The fatty acids are usually classified as saturated (carbon chain linked via single bonds), unsaturated (presence of one or more double bonds = mono and polyunsaturated, respectively), *trans* (presence of double bonds with *trans* configuration), and conjugated (presence of conjugated double bonds = a pair of double bonds separated by a single bond) fatty acids. The relative proportion of fatty acids in TAGs governs the melting behavior and thus the physical state of lipids at room temperature. While liquid oils are mainly

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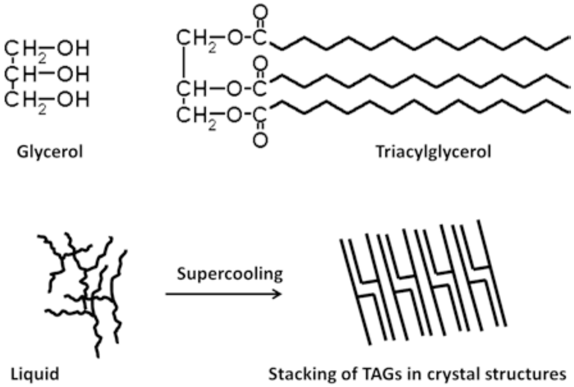


Fig. 1.1 Chemical structures of glycerol and triacylglycerol; schematic representation of the stacking of TAG molecules into organized crystal structures induced by supercooling

composed of mono and polyunsaturated fatty acids, solid fats show predominantly higher proportion of saturated and in some case, *trans*-fatty acids [1, 2].

Formulation of most lipid-based food products requires the use of solid fats to provide the necessary functionality, desirable texture as well as enhanced stability. From colloidal point of view, the crystallization and subsequent network formation of crystalline TAGs create a structural framework that can physically trap low-melting TAGs (liquid oil) into a three-dimensional gel-like structure. The crystallization of high-melting TAGs in such systems is rather complex because it is a combination of both melt crystallization due to supercooling (cooling below the crystallization temperature) and crystallization from a supersaturated state (due to the limited solubility of high-melting TAGs rich in long chain, saturated and *trans*-fatty acids in liquid TAGs which are rich in short chain, unsaturated fatty acids) [3]. In addition to this basic complication, different structural levels ranging from nanoscale to macroscale are involved in bulk fat development. The crystallization can be broadly defined by three steps: nucleation (or the formation of crystalline phase from liquid phase through organization of TAGs into a crystal lattice, Fig. 1.1), crystal growth (caused by inclusion of other TAGs from bulk liquid in the existing crystal lattice), and polymorphic transition (which governs the order of the packing of TAG molecules in the crystals) [4]. Since crystallization of fats in these systems is rather ‘slow,’ processing parameters such as rapid (quenching) and deep cooling (supercooling) along with the application of shear and incorporation of surface-active species are commonly employed to obtain the desired product. Generally, a faster cooling rate with deep cooling ensures that a large number of formed nuclei do not get enough time to grow, which, in turn, results in the formation of larger population of smaller crystals. Smaller size of crystals provides a higher overall effective surface area leading to a stronger crystal–crystal interactions in the network and a product with higher firmness. The application of shear usually facilitates nucleation (because of the enhanced rate of heat and mass transfer which may lead to the lowering of activation energy) and promotes faster crystal growth (by affecting the alignment of TAG molecules in the shear field, enhancing interparticulate collisions and/or increasing the available growth sites due to the breakage of crystals). The presence of surface-active species such as high-melting monoglycerides assists in promoting the nucleation

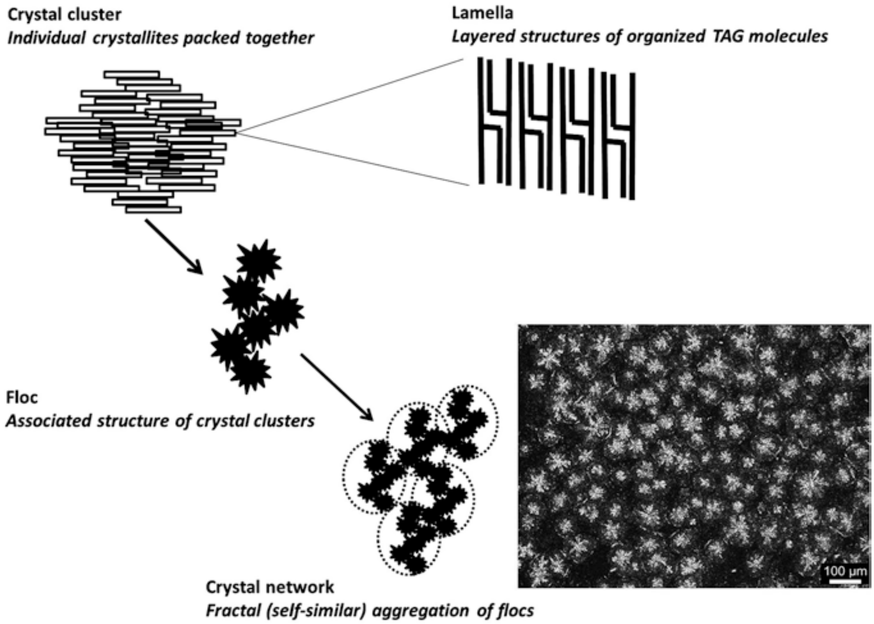


Fig. 1.2 Structural features of colloidal fat crystal network. Polarized light microscopy of structured oil system containing crystalline TAG phase (scale bar = 100 μm)

by forming stable nuclei which can act as a template for other TAG molecules to grow on. The segregated crystalline phase thus formed organizes into flocs which are linked together via weak forces to form a continuous network (Fig. 1.2).

This conventional route of structuring liquid oil currently used by lipid-based food manufacturers has certain nutritional and processing drawbacks. Since the mass fraction of crystalline phase required for structuring is quite high (≥ 0.2), the structured system contains a high proportion of solid fats [5]. In addition, the high-melting TAGs that are responsible for forming the crystalline phase are rich in *trans*- or saturated fatty acids; thus arguably, it makes the food product nutritionally poor. While the notion that excessive consumption of *trans*-fatty acid leads to negative health effects is unanimously accepted by the scientific community, same cannot be said about saturated fatty acids where contradictory views also exist [6, 7]. Nonetheless, revised guidelines from national and international health organizations have consistently advised a reduced consumption of saturated fatty acids for a long-term health. This along with the growing concern among consumers have meant that food manufacturers are actively working toward reformulation of lipid-based products with lowered amount of saturated fats and complete elimination of *trans* fats [8, 9]. However, replacing solid fats in food products is quite challenging because apart from imparting excellent organoleptic properties (melt-in-mouth effect and cooling effect), solid fats are also responsible for providing physical characteristics such as hardness, texture, crispiness, spreading, and snap. Moreover, in some food products, fat crystals also play a significant role in enhancing stability of colloidal systems by stabilizing the oil–water or air–water interfaces and increasing the bulk viscosity [10, 11]. Therefore, it is clear that if we are to replace solid fats in food products, we need to explore alternative structuring strategies (based on interdisciplinary research platforms) which go beyond the current state-of-the-art.

1.2 Oleogelation

Oleogels are a subclass of a broader colloidal systems called organogels and are simply defined as gels of organic solvents where the solvent is a liquid oil. At least from a basic research perspective, oleogelation has been hailed as an alternative oil structuring strategy that may help us formulate food products without significant amount of saturated fats in the near future. In last 6–8 years, oleogelation has changed from a relatively unheard term to a well-explored research domain as suggested from a substantial rise in the number of oleogel-related publications appearing in field-specific (food journals) as well as multi-disciplinary journals. Besides the industrial need for such an approach, the main driver for such increased interest in this area has to do with the interesting properties of oleogel systems which make them an attractive subject for interdisciplinary research. The possibility of gelling a large amount of oil solvent at a relatively lower mass fraction of gelator molecules (as low as 0.5 wt% in some cases) makes oleogelation a very efficient means for structuring oil in the absence of solid fats. This efficient structuring in oleogels is typically achieved by supramolecular assemblies (building blocks) of gelator molecules that organize into a 3D network, trapping a large amount of oil into a gel-like structure [3, 5, 12, 13].

Over the last decade, a number of gelator molecules have been researched for edible oil structuring (see Fig. 1.3), the basic building blocks (supramolecular assemblies) formed by these molecules fall into one of the following categories: (a) crystalline particles; (b) self-assembled structures of low molecular weight compounds (fibers, strands, tubules, reverse micelles, mesophases, etc.); (c) self-assembled structures of polymers or polymeric strands, and (d) miscellaneous structures such as colloidal inorganic particles and emulsion droplets. The building blocks can be formed by single component or mixture of components (mixed systems), and the formation of building blocks could be achieved through direct method (usually by dispersing gelator molecules in oil medium at high temperatures followed by cooling) or indirect method in case of hydrophilic polymers (where dried microstructures are created by stripping-off the water from hydrated polymer solutions). A brief discussion on these gelator molecules is summarized below:

1.2.1 *Crystalline Particles and Self-Assembled Structures of Low Molecular Weight Compounds*

1.2.1.1 Mono- and Di-acylglycerols

As an alternative to TAGs, glycerol esters of fatty acids such as mono- and di-acylglycerols (MAGs and DAGs) that are known to show somewhat similar

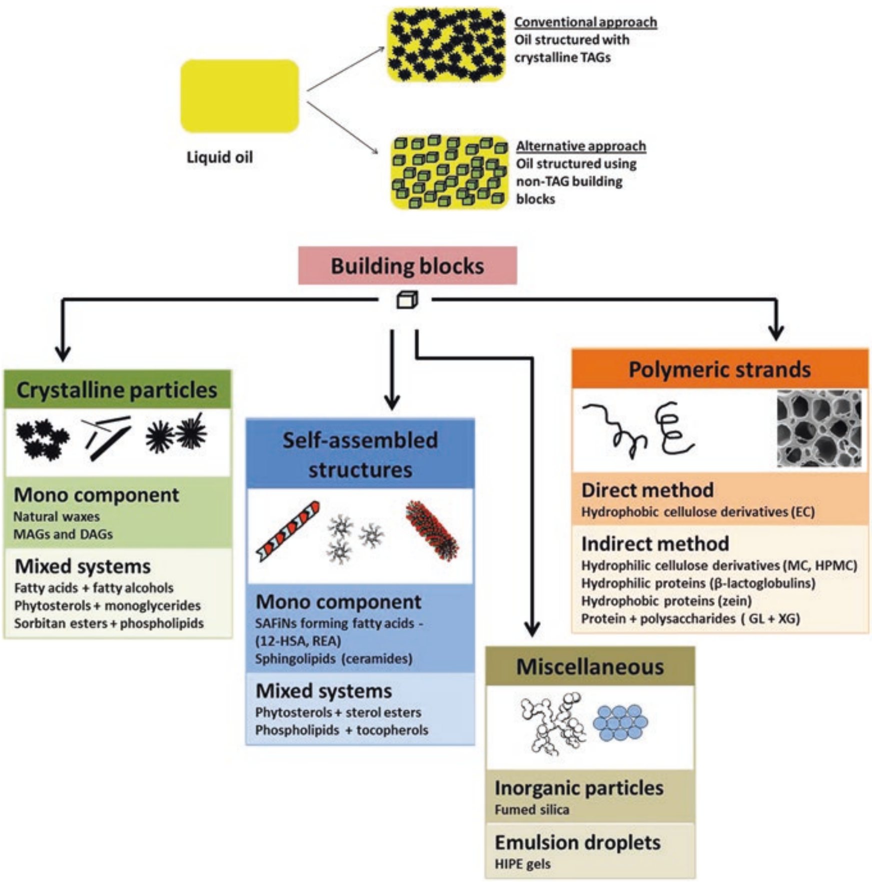


Fig. 1.3 Schematic representation of conventional and alternative approaches for oil structuring and categorical listing of building blocks which can be used for oil structuring. Reprinted from Patel and Dewettinck [53]

crystallization properties to TAGs have been explored for structuring of edible oil. The advantage of using these partial glycerides (particularly, DAGs) over TAGs is that while they can mimic the crystal network formation and temperature-induced texture reversibility shown by TAGs, their digestion in the GI tract is quite different from that of TAGs and does not follow the usual mucosal resynthesize of TAGs, resulting in decreased body fat accumulation [14, 15]. Moreover, the unesterified, free hydroxyl group(s) on glycerol backbone makes them more polar compared to TAGs and the resultant self-assembling properties ensure a more efficient structuring of oil (Fig. 1.4) at much lower concentrations than TAGs [13, 16–18]. Particularly, in case of MAGs, there is also a possibility of incorporating a large amount of water which can be considered as a distinct advantage since many food products are biphasic colloids containing oil and water phases [19, 20].

Fig. 1.4 (*On left*) Monoglyceride-based oleogel containing 95 wt% sunflower oil; (*on right*) polarized light microscopy image showing the crystalline network formation in the oleogel (scale bar = 100 μm)

1.2.1.2 Natural Waxes

Among molecules forming crystalline particles, natural waxes (most of which are food-approved albeit only for specific applications) are by far the most studied group of compounds for edible oil structuring. Chemically, waxes are composed of multiple chemical entities such as wax esters, fatty acids, fatty alcohols, and linear hydrocarbons [21, 22]. Because of the presence of molecular units with linear structures, crystals formed by waxes show predominantly higher 1D and 2D growth (proportionally a lower lateral growth) resulting in needlelike to platelike structures which are more efficient at gelling a polar solvents at much lower crystalline mass fractions, such that, even a concentration of lower than 2 wt% is sufficient to transform liquid oils into viscoelastic gels with interesting rheological properties [23, 24]. In addition, because of the presence of surface-active components such as fatty alcohols in waxes, the structured oleogel systems can also be used as oil phase for fabricating surfactant-free emulsions (Fig. 1.5). The water droplets are further stabilized by interfacial accumulation of fine wax crystals (i.e., Pickering stabilization) [24].

1.2.1.3 SAFiNs Forming Fatty Acids

Hydroxylated fatty acids such as 12-hydroxy stearic acid (12-HSA) [25] and its derivative 12-hydroxy, 9 *trans*-octadecenoic acid (ricinelaidic acid, REA) [26] show interesting properties of forming self-assembled fibrillar networks (SAFiNs) that can provide a structural framework to trap a large volume of solvent, resulting in the formation of organogels (Fig. 1.6). The efficient gelation of solvent by hydroxylated fatty acids is attributed to unidirectional crystal growth resulting in highly anisotropic (high aspect ratio), fibrous crystalline strands which can be a few micrometers in length. The gels formed by SAFiNs are usually transparent to translucent in appearance and display strong birefringence when viewed under polarized light [27]. Transparent gels

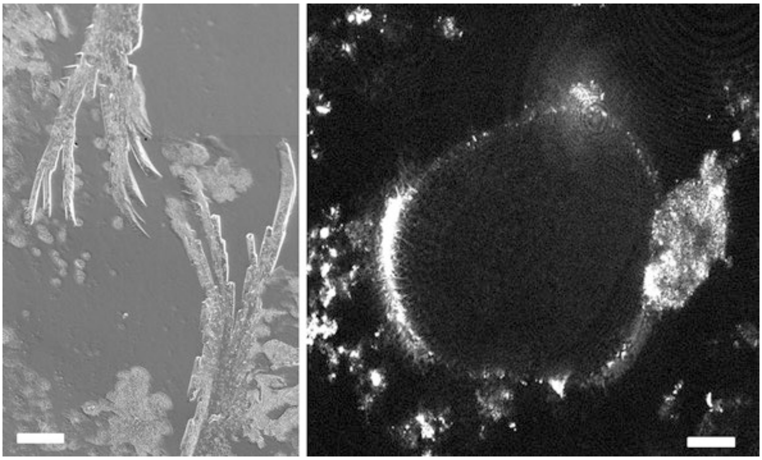
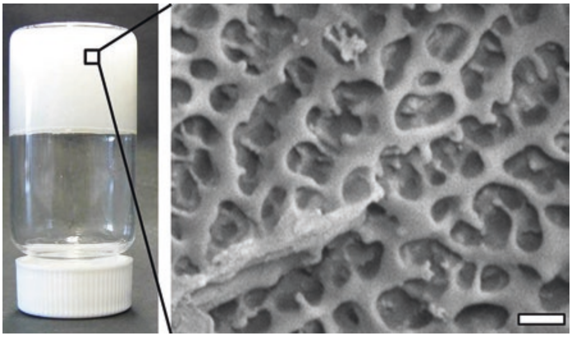


Fig. 1.5 (*On left*) Needle-like crystals of wax (sunflower wax) seen under cryo-SEM (scale bar = 20 μm); (*on right*) confocal image (taken in reflectance mode) of oleogel-based emulsion showing the accumulation of fine wax crystals (shellac wax) at water–oil interface (Pickering stabilization), scale bar = 30 μm

Fig. 1.6 (*On left*) 12 HSA-based oleogel containing 98 wt% sunflower oil; (*on right*) cryo-SEM image of oleogel showing a continuous network of self-assembled structures with a nanoscale mess size (scale bar = 100 nm)



can be formed at very low concentration of gelator molecules (as low as 0.5 wt%) due to the entanglement of fibrous strands, and as the concentration is further increased, transient junction zones (microcrystalline domains) are formed between fibers which results in an increased fiber clustering and opacity of the gels [28].

1.2.1.4 Sphingolipids

Sphingolipids are a class of biologically relevant lipids containing a sphingosine (a type of aliphatic amino alcohol) backbone with either one hydroxyl group esterified to a fatty acid side chain (ceramides) or both hydroxyl group substituted with a fatty acid and a non-fatty acid group (sphingomyelin, cerebroside, and ganglioside). The oil gelling properties of ceramides (which are the simplest of sphingolipids) were studied using synthetic ceramides and ceramides derived from egg sphingomyelins [29]. The gelation mechanism in ceramide oleogels was postulated to follow the nucleation–crystal growth–branching–crystal growth model, and it was further apparent that the melting behavior and the rheology of the gels could be varied by using ceramides differing in the length of the fatty acid side chains. However, gels formed at concentrations as high as 10 wt% of ceramide were rheologically classified as weak gels [29].

1.2.1.5 Mixed Systems

While the different classes of gelator molecules described above are capable of forming stable oleogels on their own, there are many other gelator molecules (fatty acids, phospholipids, phytosterols, etc.) that are not as efficient at producing stable oleogel when used alone. It has been found that the microstructure of gels comprising of the molecular assemblies formed by these components (crystals or self-assembled structures such as reverse micelles and SAFiNs) can be influenced and strengthen by incorporation of another component that may or may not show similar self-assembly behavior. In fact, in some cases (such as stearic acid + stearyl alcohol), a clear synergistic effect has been noticed [30]. The improvement in the gelation properties was attributed to the combined crystallization of two components, resulting in crystals that had a completely different morphology compared to the crystals of single components (needle-like crystals for mixtures compared to plate-like crystals for individual components) [31]. A combination of phytosterols and sterol esters (in particular, β-sitosterol + γ-oryzanol) has been researched quite extensively for oil structuring, and the building blocks in these oleogels are self-assembled tubules of nanoscale dimensions (diameter ≈ 7.2 nm, thickness ≈ 0.8 nm). These tubules have a complex helical, ribbonlike structure which is mediated by the intermolecular H-bonding between the hydroxyl group of sitosterol and carbonyl group of oxyzanol [32]. Although the combination is able to form clear (or slightly hazy) oil gels, the effectiveness of structuring in the presence of water becomes less because of the formation of much thicker sitosterol monohydrate fibers (microscale dimensions) [33].

Recently, we also identified synergistic effect when saturated and unsaturated MAGs were combined with commercial phytosterols, PS (containing at least 40 % sitosterols) at certain ratios. As discussed earlier, crystalline particles formed by MAGs can connect together to form a 3D network that results in oleogel formation. However, these oleogels are usually soft in nature (low firmness) and we also found that MAGs are prone to polymorphic transition over time, resulting in the formation of grainy crystals (Fig. 1.7a). On the other hand, PS crystallize as large flat crystals (Fig. 1.7b) and thus form weakly structured oleogels that are prone to phase separation caused by aggregation-induced contraction of crystalline phase. Surprisingly, by combining MAGs with PS at certain proportions (and a total gelator concentration of 10 wt%), a synergistic enhancement in the rheological properties of oleogels was observed due to the formation of finer crystalline particles with completely different morphology compared to MAG and PS crystals (Fig. 1.7c). In addition, based on a 4-week storage study, it was confirmed that the contraction of

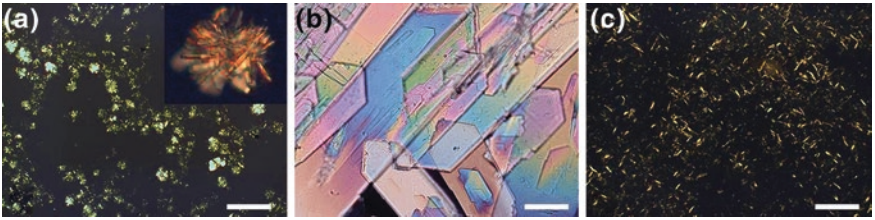


Fig. 1.7 Polarized microscopy images of crystalline structures observed in oleogels prepared using 90 wt% sunflower oil and 10 wt% of (**a**) DM (distilled MAGs from palm oil); (**b**) PS and (**c**) DM:PS, 6:4 (scale bars = 100 μm). Notice how the DM and PS crystallize into grainy polymorph (*inset a*, image width = 50 μm) and flat plate-like crystals, respectively, whereas, when these components are used in combination, finer crystalline particles are formed which are completely different from DM and PS crystals

crystalline phase and consequent phase separation was also prevented. This is first such demonstration of identifying synergistic combination that can overcome drawbacks associated with individual structurants (unpublished results).

Aside from the above-mentioned components, other mixed systems such as lecithin + sorbitan tristearate; lecithin + sitosterol; and lecithin + α-tocopherol have also been explored where lecithin can contribute as crystal modifier, network strengthener (formation of weak junctions between crystals), and stabilization of complex micellar structure [34–36].

1.2.2 Self-Assembled Structures of Polymers or Polymeric Strands

1.2.2.1 Ethyl Cellulose-Based Oleogels

Ethyl cellulose is a hydrophobic cellulose derivative chemically synthesize from cellulose through substitution of hydroxyl group on monomeric glucose units forming the backbone of cellulose. The properties of EC (as well as other cellulose derivatives) are dependent on degree of polymerization (DP) and degree of substitution (DS). While DP gives a measure of the molecular weight of the polymer, DS gives information about the number of OH substituted. Since glucose monomers have 3-OH groups that can be substituted, the DS varies between 0 and 3. Based on the DP and DS, various viscosity grades of EC are available. Although the use of EC for gelation of vegetable oils was already reported many years ago [37, 38], the relevance to food applications has been extensively demonstrated by Marangoni's group [39, 40]. EC-based oleogels are usually prepared by dispersing polymer powder in liquid oil under shear at temperatures above the glass transition temperature of EC ($T_g \approx 130$ °C) followed by cooling to lower temperatures. At high temperatures, the polymer chains are unfolded, and on subsequent cooling, the unfolded polymer chains form a backbone for cross-linked gel network. The gel is stabilized by hydrogen bonding among polymer chains along with some hydrophobic interactions between acyl chains of oil and the side chains of ethyl cellulose [41].

1.2.2.2 Polymer-Based Oleogels Prepared Using Indirect Methods

Hydrophilic polymers such as polysaccharides and proteins have long been used as structuring agents for creating aqueous gels. Since water acts as a good solvent for these polymers, the polymer–solvent interactions dominate, and consequently, the hydrated polymeric molecules (random coils) can acquire unfolded extended shapes. If these random coils are considered as rigid spheres, as the polymer concentration exceeds a certain concentration (C^*, overlap concentration), these rigid spheres start overlapping (polymeric molecules start interacting weakly), leading to an increase in the slope of specific viscosity *versus* concentration curve. Beyond this overlap concentration, addition of further polymer molecules is accompanied with a higher polymer–polymer interactions and a strong interpenetration of polymer molecules. Above C^*, a critical cross-linking concentration (also known as critical gelling concentration, C_g) may be achieved where a three-dimensional cross-linked structure (stabilized by cross-linked junction zones) and the gelation of solvent occurs [42, 43].

When it comes to oils, it is not possible to disperse hydrophilic polymers in hydrophobic solvents as they do not possess the matching solubility characteristics. However, some of these hydrophilic polymers (proteins and modified polysaccharides) are known to have surface activity due to the presence of hydrophobic groups in their molecular structures. Thus, in principle, structural frameworks of polymers can be created by forcing the hydrated polymers to accumulate at the air–water or oil–water interfaces followed by stripping-off the water. Such indirect methods using colloids with air–water interfaces (aqueous foams) [44] or oil–water interfaces (water continuous emulsions) [45, 46] as templates have been utilized to create dried microstructure of hydrophilic polymers (such as hydroxypropyl methylcellulose, β-lactoglobulins, gelatin + xanthan gum (GL + XG), and methylcellulose + xanthan gum) which can be used for structuring liquid oils. One modification of such indirect approach has also been explored where Pickering emulsions (stabilized by nanoparticles of hydrophobic protein-zein) were used as templates [47].

Polymer-based oleogels (prepared by direct or indirect approaches) hold significant promise in the area of edible oil structuring because of the availability of a wide range of polymers (proteins and polysaccharides) which are cost-effective as well as food-approved. More detailed discussion on oil structuring using hydrophilic polymer can be found later in the book (Chap. 3).

1.2.3 Miscellaneous

1.2.3.1 Inorganic Particles

The use of inorganic particles of clay and amorphous silica as structuring agents to form gels in aqueous and organic solvents is well documented [48]. The gelation mechanism involves a long-range organization of colloidal particles into mesoscopic structures that further associate to form very large fractal superaggregates [49, 50]. In our laboratory, we recently explored the possibility of using fumed silica (Aerosil®) as a structurant for gelling sunflower oil. Surprisingly, hydrophilic silica (Aerosil®

150) displayed better gelation properties compared to hydrophobic silica (Aerosil® R972). Moreover, it was observed that the structured oleogels can be combined with weak water gels to obtain a relatively less-explored class of colloids called bigels. More details about fumed silica-based oleogels and bigels are described in Chap. 4.

1.2.3.2 Emulsion Droplets (HIPE Gels)

High internal phase emulsions (HIPEs) are defined as concentrated emulsion systems where the volume fraction (φ) of dispersed droplet phase is above 0.74. The high population of dispersed droplets results in close packing of deformed droplets separated with a thin film of continuous phase [51]. Recently, HIPEs were used as templates to create oil continuous gels using low-temperature-triggered gelation of closely packed water droplets [52]. The HIPEs were prepared using an aqueous phase (structured using locust bean gum and carrageenan at varying ratios and a total concentration of 1 wt%) at volume fraction above 0.74 and polyglycerol polyricinoleate (at 0.4 wt% of total emulsion) as lipophilic emulsifier. A pictorial representation of the preparation process is shown in Fig. 1.8, and the gelling of water droplets was achieved through temperature-triggered gelation of locust bean gum and carrageenan combination. The network of closely packed gelled water droplets provides a structural framework which supports the oil continuous phase, leading to the formation of a self-standing gel. The microstructure studied using confocal microscopy confirms the close packing of water droplets. Further, the polyhedral microstructure of dispersed phase

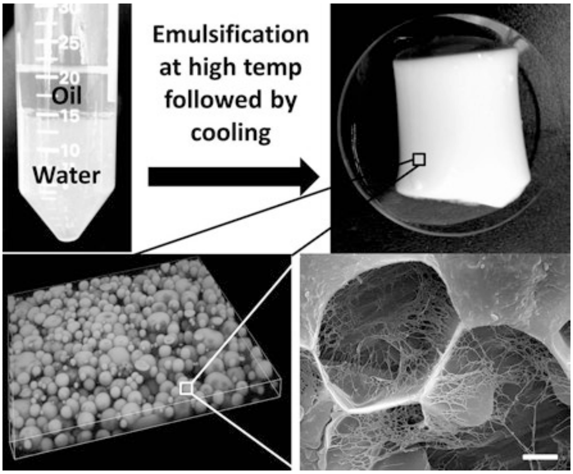


Fig. 1.8 Pictorial representation of process used for HIPE gel formation. The microstructure of the gel was visualized using confocal microscopy (using water soluble fluorescent dye) and cryo-SEM. The volume view (created by staking images from confocal microscope, dimensions, x = 212 μm, y = 212 μm and z = 15 μm) image confirms that the dispersed water droplets are jammed together in an oil continuous medium, and the cryo-SEM image (scale bar = 1 μm) taken after sublimation of freeze-fractured sample clearly shows the presence of polymer network responsible for gelation of eater droplets which are packed together in a hexagonal packing. Figure adapted from [52, 53]

droplets can be also clearly seen in the cryo-SEM image of freeze-fractured sample. A polymeric framework left behind after sublimation of water can also be seen in the image. The HIPE gels showed many interesting rheological properties; particularly, the thermo-reversible texture changes as the samples undergo gelsol transformation at high temperatures (>50 °C) without showing any droplet coalescence. The important requirement for this approach is the right selection of hydrocolloids. Firstly, the selected hydrocolloids should show a thermo-reversible gelation (setting at low temperature and melting at higher temperatures), and secondly, the hydrocolloids should be non-surface active in order to prevent the formation of water continuous gels.

1.3 Conclusions

The conventional approach for structuring oil that is currently used in the food manufacturing industries relies on the use of crystalline TAGs as the building blocks. Since these high-melting TAGs are rich in *trans*- and/or saturated fatty acids, the nutritional profile of such structured oil systems is unhealthy, and from a processing point, structuring with this approach requires higher crystalline mass fraction (≥ 0.2 or 20 wt%). In addition, due to the complexity involved in structuring, processing parameters (such as temperature–time profiling) need to be carefully controlled to achieve desired results. As discussed above, alternative approaches that are based on the use of newer building blocks as structurants could be explored to achieve efficient structuring at much lower concentrations. Moreover, some of the structuring components such as DAGs are known to have nutritional benefits over TAGs, while agents belonging to the class of phytosterols and sphingolipids are themselves known to interfere with cholesterol absorption in the intestine. In addition, some of the components such as waxes, cellulose derivatives, and fumed silica are non-digestible and hence non-calorigenic. However, it is important to remember that we still have a long way to go before the commercial applications of alternative approaches can be realized. There are certain drawbacks which need to be considered such as the sensitivity of oleogels to shear (low thixotropic recovery), structure collapse in the presence of water, and time-dependent changes in the rheological properties of some systems (particularly, wax-based oleogels). In addition, there are regulatory restrictions related to the use of some structuring agents (such as some natural waxes, 12-HSA, and fumed silica) as direct additives for food applications.

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Chapter 2
Natural Waxes as Oil Structurants

Abstract Wax-based oleogels display very interesting and complex rheological behavior; the physical gels of liquid oils created using natural waxes can be assumed to have characteristics of both the flocculated suspensions and semi-dilute polymer solutions. In this chapter, a comparative evaluation of six different natural waxes (with differing melting ranges) is described mainly with respect to their network forming properties at their respective minimum gelling concentrations to give the readers a comprehensive understanding of wax-based oleogels.

Keywords Wax-based oleogels · Rheology · Microstructure · Cryo-SEM · Small amplitude oscillatory shear · Crystallization

2.1 Introduction

Among various structurants that are so far explored for gelling vegetable oils, natural waxes are considered to be the most promising ones because of their excellent oil-binding properties [1], economical value (capable of gelling oils at significantly lower concentrations, as low as 0.5 %wt) [2], and availability of a number of waxes that are approved for use in foods (albeit as indirect additives) [3, 4]. Moreover, gels formed using waxes have interesting properties such as thermo-reversibility (gelsol transition as a function of temperature) [5, 6] and stabilization of water-in-oil emulsions [7–9], which further justifies their popularity as structuring agents for edible oils.

The enormous potential of waxes has been appreciated by many research groups and accordingly, the gelation behavior of waxes has been studied extensively with respect to the chemical properties of waxes (composition and impurities) [2], thermodynamics and kinetic aspects of wax crystallization (fractal aggregation, thermal properties, crystal morphology, and cooling rates) [1, 10, 11], and bulk response of gels to small and large deformations (rheology and texture analysis) [12–14].

In this chapter, a comparative evaluation of six different natural waxes (with differing melting ranges) is described mainly with respect to their network forming properties at their respective minimum gelling concentrations to give the

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Table 2.1 Chemical composition of selected waxes

Waxes	Chemical composition (%wt)			
	HCs	WEs	FAs	FALs
SFW	0.17 ± 0.16	96.23 ± 0.19	3.29 ± 0.16	0.32 ± 0.38
CRW	0.41 ± 0.30	62.05 ± 3.03	6.80 ± 0.76	30.74 ± 2.48
CLW	72.92 ± 2.23	15.76 ± 0.35	9.45 ± 1.14	2.20 ± 1.02
BZW	26.84 ± 1.04	58.00 ± 0.68	8.75 ± 0.75	6.42 ± 0.90
BW	<0.05	<0.05	95.70 ± 1.11	4.24 ± 1.10
FW	0.83 ± 0.16	0.24 ± 0.01	36.43 ± 7.19	62.50 ± 7.03

readers a comprehensive understanding of wax-based oleogels. A more meaningful rheological characterization was made possible in this study since we used gels prepared at the respective minimum gelling concentrations of waxes.

Chemically, waxes comprise of multiple chemical entities include wax esters (WEs), hydrocarbons (HCs), fatty acids (FAs), and fatty alcohols (FALs) as the main components. Because of this multi-component nature, waxes show melting ranges instead of definite melting points and depending on the proportion of major components, different waxes show variation in their melting ranges. To get a comprehensive view, six waxes differing in their chemical compositions were selected as follows: Sunflower wax, *Helianthus Annuus Seed Cera* (SFW); Carnauba wax, *Copernicia Cerifera Cera* (CRW); Candelilla wax, *Euphorbia Cerifera Cera* (CLW); Bees wax, *Cera Alba* (BZW); Berry wax, *Rhus Verniciflua Peel Cera* (BW); and Fruit wax, *Myrica Cerifera* (FW). The relative proportions of different chemical components in these waxes are tabulated in Table 2.1.

The gelling properties of these waxes were compared based on the minimum gelling concentrations (C_g), thermal properties (crystallization), microstructure studies, and rheological properties of oleogels formed at C_g of respective waxes.

2.2 Minimum Gelling Concentration and Microstructure

Wax-based oleogels are prepared using a straightforward dispersion method. The liquid dispersion of wax in oil is heated above the melting range of the wax until the solid wax particles are completely melted. The hot, clear oily dispersion is then cooled to low temperature (5 °C) under continuous stirring. Since not all waxes show immediate gelation on cooling, it is advisable to store the cooled oily dispersion at 5 °C for certain duration of time to evaluate the gelation behavior of the wax. In the current study, to identify the C_g (Table 2.2), a series of oily dispersions were made by varying the concentration of waxes and heating them at 90 °C and subsequently cooling the dispersion to 5 °C. The gelation was noted first by simple tube flipping observation to identify the concentration ranges where the gels did not flow under the influence of gravity, followed by oscillatory rheological

Table 2.2 Critical gelling concentration (C_g) and crystallization onset (T_c onset) and peak (T_c peak) temperatures (mean ± SD) for waxes in oleogels prepared at their respective C_g in high oleic sunflower oil (HOS)

Waxes	C_g (%wt)	T_c onset (°C)	T_c peak (°C)
SFW	0.5	57.27 ± 0.05	55.97 ± 0.31
CRW	4	54.61 ± 0.05	52.83 ± 0.44
CLW	0.75	38.72 ± 0.82 (I)	37.76 ± 0.84 (I)
		34.06 ± 0.12 (II)	31.14 ± 0.42 (II)
BZW	1	42.69 ± 0.35	40.98 ± 0.75
BW	6	8.92 ± 0.41	6.27 ± 0.03
FW	7	14.87 ± 0.11	10.55 ± 0.07

measurements (amplitude sweeps) to distinguish between a gel ($G' > G''$) and a viscous sol ($G'' > G'$) under low applied shear (τ_o), where G' and G'' are elastic and viscous modulus, respectively.

Among the studied waxes, SFW, CLW, and BZW were found to be more efficient gelators, capable of forming gels at significantly lower concentrations ($C_g \leq 1$ %wt). On the other hand, waxes such as BW and FW required much higher concentrations (6 and 7 %wt, respectively). The higher C_g values for BW and FW are understandable because these waxes are devoid of components with larger 'carbon backbone'; they are mainly composed of low melting short chain FAs ($C_{14:0}$, $C_{16:0}$, $C_{18:0}$) and FALs ($C_{20–22}$). The relatively higher solubility of these low melting components is also confirmed from the crystallization peaks of BW and FW oleogels as shown in Fig. 2.1a, where the peaks are shifted to much lower temperatures compared with the peaks of neat waxes (data not shown).

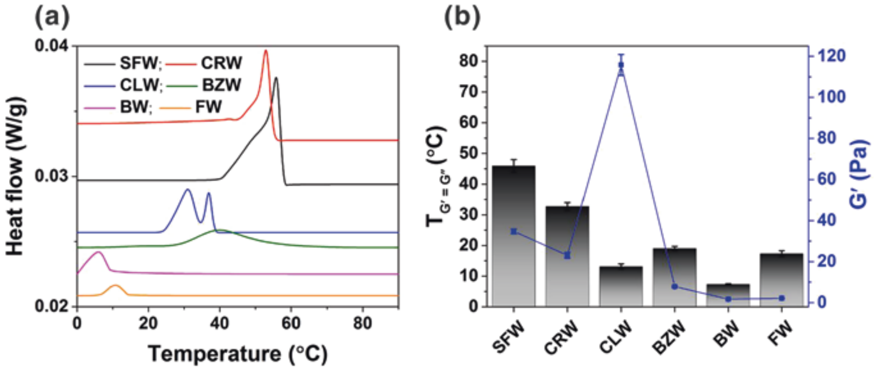

Fig. 2.1 **a** Comparative cooling *curves* of oleogels prepared at C_g of respective waxes in HOS; **b** Gelation temperature ($T_{G' = G''}$) and elastic modulus (G′) at crossover point for oleogels prepared at C_g of respective waxes in HOS

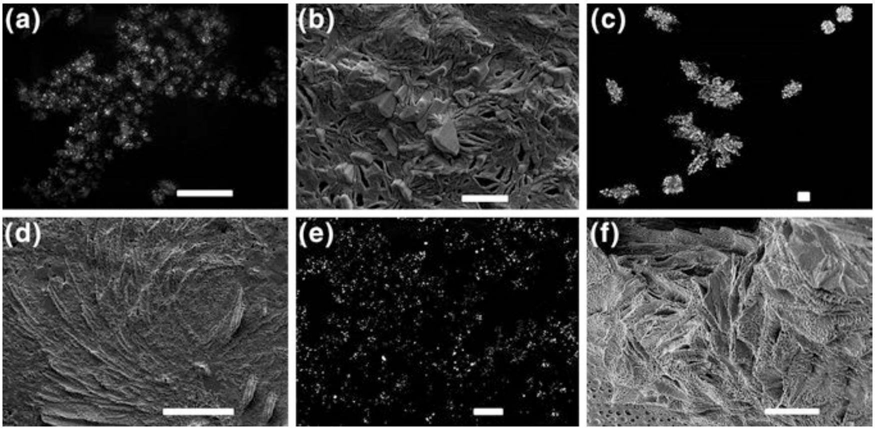

Fig. 2.2 Polarized light microscopy and cryo-SEM images of oleogels of **a**, **b** BW; **c**, **d** FW; and **e**, **f** CLW. Scale bars = 50 μm (**a**, **e**); 20 μm (**c**); 10 μm (**d**); and 1 μm (**b**, **f**). Adapted from Patel et al. [32]

To understand the relationship between crystallization and gelation, a single-frequency test was done on samples where the material functions (G' and G'') were measured as a function of temperature (at constant stress, $\tau = 0.02$ Pa and frequency, $\nu = 1$ Hz). The temperature ($T_{G'=G''}$) and G' at the crossover point (or sol-gel transformation point) for oleogel samples prepared at C_g of the individual waxes are shown in Fig. 2.1b. For SFW, CRW, CLW, and BZW samples, a prominent delay in gelation was evident with $T_{G'=G''}$ being much lower than the peak crystallization temperature (T_c peak), while gelation and crystallization occurred simultaneously for BW and FW samples (Fig. 2.1b and Table 2.2). On comparing the G' values for the gels at their respective crossover points, it can be speculated that gelation of BW and FW gels ($G' < 2.5$ Pa) is not preceded by extensive microstructure development unlike the samples of SFW, CRW, CLW, and BZW. The FAs in BW and FW are esterified to glycerol backbone and these nonlinear molecules display lateral packing and consequent formation of large 3D crystals. Due to the formation of relatively larger spherical crystal/crystalline aggregates (Fig. 2.2a–d) by BW and FW (along with a comparatively higher crystalline weight fractions), the possibility of creating loose entanglements is higher. These entanglements can act as transient junction points which can contribute to the elasticity but sustain only a very low magnitude of stress as confirmed from amplitude and frequency sweeps discussed later in the text. The platelet-like crystals are clearly distinguishable in spherical crystalline aggregates of BW (Fig. 2.2b), while flat crystals are seen radiating outward from the center to form spherical units in case of FW (Fig. 2.2d).

Among other four waxes, the most striking results were observed for CLW gel where the G' at crossover point was exceptionally high (≈115 Pa) while the gelation occurred only after completion of crystallization, strongly suggesting that gel formation is a result of a significant reorganization of crystalline phase at lower

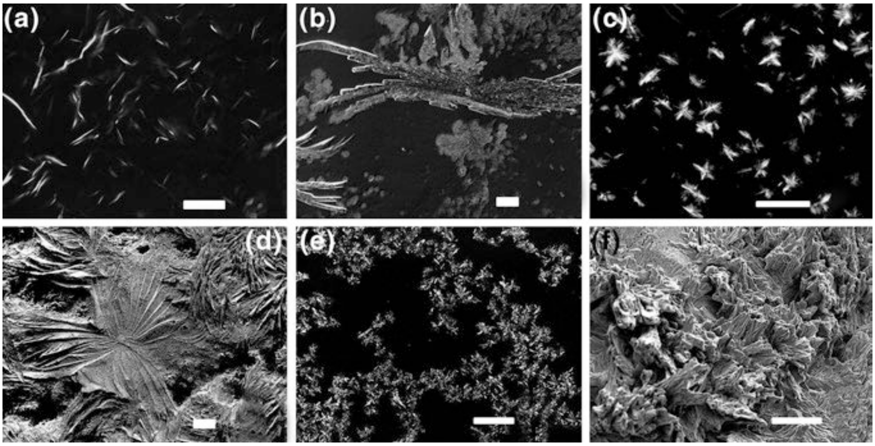

Fig. 2.3 Polarized light microscopy and cryo-SEM images of oleogels of **a**, **b** SFW; **c**, **d** BZW; **e**, **f** CRW. Scale bars = 50 μm (**a**, **e**); 20 μm (**c**); 10 μm (**b**, **f**); and 1 μm (**d**). Adapted from Patel et al. [32]

temperatures (higher super cooling). As shown in Fig. 2.2e, f, CLW crystallizes into very fine linear particles that are further organized into an open aggregate-like structures. The sparse (non-compacted) packing is also evident from a low birefringence in PLM images. The formation of such crystalline particles by CLW is attributed to a high proportion of linear hydrocarbons (*n*-alkanes) as reported previously [15]. In addition, the formation of gels with higher elasticity at lower crystalline mass fraction is in agreement with previously reported studies on CLW-oil oleogels [6, 16].

Further, the differences in C_g for SFW and CRW (0.5 and 4 %wt, respectively) can be explained from the morphology of crystals formed in these two gels (Fig. 2.3a, b, e, f). SFW crystals had anisotropic, rod-like morphology (with lengths spanning in the micrometer range). The rod-like morphology of SFW is attributed to its high content (>95 %wt) of wax esters which are known to be the main components responsible for excellent gelation behavior of most natural waxes [1, 2, 11]. Such morphology is considered to be the most desirable shape of elementary assemblies (building blocks) to immobilize a large volume of solvent for efficient gelation [17]. In contrast, in CRW gels, the three-dimensional crystals of less than 10 μm in size are seen stacked closely together into larger aggregates (50–100 μm) and thus, a relatively higher crystalline mass fraction is required for gelation because the network formation occurs due to the overlapping of spherical volumes of these aggregates as against the spherical volumes of linear assemblies as seen in SFW.

Interestingly, the crystal structure in BZW gel was quite different from other waxes, showing a distinct ‘sea urchins’-like morphology (Fig. 2.3c, d). Formation of such interestingly organized structures has been explained through crystal design and engineering and is attributed to a two-stage crystallization process initiated by a three-dimensional spherulite formation at the nucleation center followed by the organization of needle-like crystals in the outer layer resulting in a radially oriented growth [18].

2.3 Rheological Characterization

2.3.1 Small Amplitude Oscillatory Shear (SAOS)

Oscillatory measurements offer a convenient way of measuring the flow and deformation properties of viscoelastic samples and also facilitate the classification of samples into strong gels, weak gels, and viscous sols based on amplitude and frequency sweeps [19].

Typically, for gels, the elastic component dominates (G') over viscous component (G'') at small applied shear and attains a plateau (G'_{LVR}) in the linear response region (LVR or linear viscoelastic region) [20]. The end of LVR is marked by the first point where the G' varies by 10 % of the G'_{LVR} value and the corresponding stress at this point is referred to as the critical stress (τ^*). As the applied shear increases further, a permanent deformation (yielding) of the materials may occur ($G' = G''$) and the corresponding stress value at this point is referred to as oscillatory or dynamic yield stress (τ_{dy}) [21]. The τ^* represents the onset of nonlinearity (and hence structure breakdown), while τ_{dy} represents the transition from solid- to liquid-like behavior and the zone spanning of these two events is referred to as the yield zone [22, 23].

The plots from amplitude and frequency sweeps done on organogels are shown in Fig. 2.4. As seen from the graphs, none of the studied samples satisfied the rheological definition of a 'strong gel' (G''/G' (ω) ≤ 0.1). However, CRW gel did show least frequency dependence (more or less linear curve in Fig. 2.4b), higher G'_{LVR} value, and higher oscillatory or dynamic yield stress (τ_{dy}) in comparison with other gels. As discussed earlier, the elasticity of BW and FW organogels is attributed to loose entanglements of large crystals and because of this structure, the gels can only sustain lower magnitude of stress which is confirmed from low values of dynamic moduli in the linear response region. Moreover, these gels also showed a very low

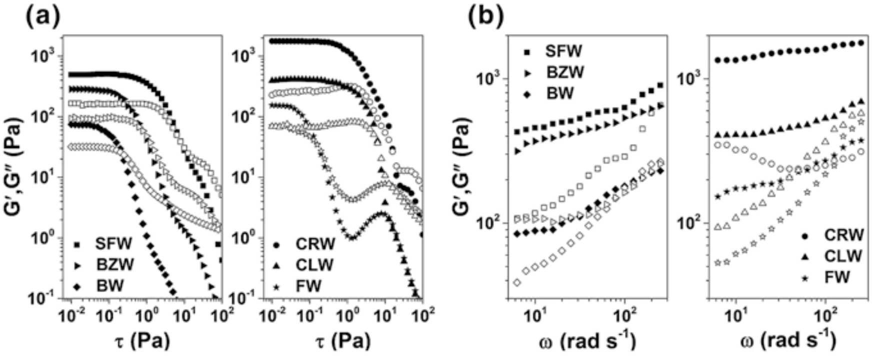

Fig. 2.4 **a**, **b** Amplitude (at frequency, $\nu = 1$ Hz) and frequency (at stress, $\tau = 0.02$ Pa) sweeps for gels made at C_g of respective waxes. G′ and G″ are shown as filled and open symbols, respectively, and frequency is plotted as angular frequency, $\omega = 2\pi\nu$

values of critical stress, τ^* (<0.05 Pa) and a narrow yield zone with τ_{dy} (<0.25 Pa). The slope of curve in the yield zone gives information about the breakage of intermolecular forces holding up the structure, and a narrow yield zone points at the fact that the structure breakdown occurs at once (all bonds break at the same force).

The weak structure of BW and FW gels is further evident from a prominent crossover ($\tan\delta = G''/G' > 1$) at higher ω, which is a confirmation of structure breakdown at high rates of deformation. SFW gel was much softer than CRW and yielded at much lower force (dynamic yield stress, $\tau_{dy} = 9.9$ Pa compared to 19.8 Pa for CRW gel). Both CLW and BZW gels showed similar frequency dependence but the gel formed by BZW was comparatively more brittle and showed breakdown and yielding at lower stress values.

2.3.2 Flow Behavior

The yielding-type behavior with a strong shear thinning nature of all the gels is evident from the curves of complex viscosity (η^*) plotted as a function of ω as well as from the graphs of apparent viscosity (η_{app}) versus shear rate ($\dot{\gamma}$) as shown in Fig. 2.5a. Flow parameters such as apparent yield stress (${}_{app}\tau_y$) and flow index (n) were calculated by fitting the data to a three-parameter model (Hershel Bulkley, Eq. 1).

$$\tau = {}_{app}\tau_y + K\dot{\gamma}^n \qquad (1)$$

where K = consistency coefficient and $\dot{\gamma} =$ shear rate.

The Hershel Bulkley model is one of the most commonly used models for characterizing materials that display non-Newtonian behavior after yielding and the value of n can be used as a measure to define the degree of shear thinning ($n < 1$) or shear thickening ($n > 1$) of the material. All the samples showed a prominent shear thinning flow behavior ($n < 1$), but the degree of shear thinning was highest for CRW gels which incidentally also had the highest ${}_{app}\tau_y$ (Table 2.3). In addition, CRW gel also showed a highest static yield stress (τ_{sy}) determined from the plots of stress ramp (Fig. 2.5b). The τ_{sy}, measured using methods such as stress ramp and stress growth, is defined as the minimum stress required for initiating flow, whereas, the ${}_{app}\tau_y$, determined by model fitting, is defined as the minimum stress required for maintaining flow and is often lower in values than former [23–26]. τ_{sy} and ${}_{app}\tau_y$ for all the gels were close to each other except for CRW gel where τ_{sy} was almost three times larger than ${}_{app}\tau_y$. Such big difference in stresses required for initiating and maintaining flow is taken as an indication of the existence of more than one structure that makes up the body of a material [23, 26]. One of these structures is built up only during rest and can undergo breakdown under relatively lower shear, while a more robust structure that can withstand moderate shear rates contributes to the ${}_{app}\tau_y$ [25, 26]. Since τ_{sy} is a consequence of combined structures, it is expected to be higher than ${}_{app}\tau_y$. The high zero-shear viscosity of CRW gel (Fig. 2.5a) confirms that network structure is built up by overlapping spherical volumes of large aggregates and a strong shear thinning behavior is a consequence

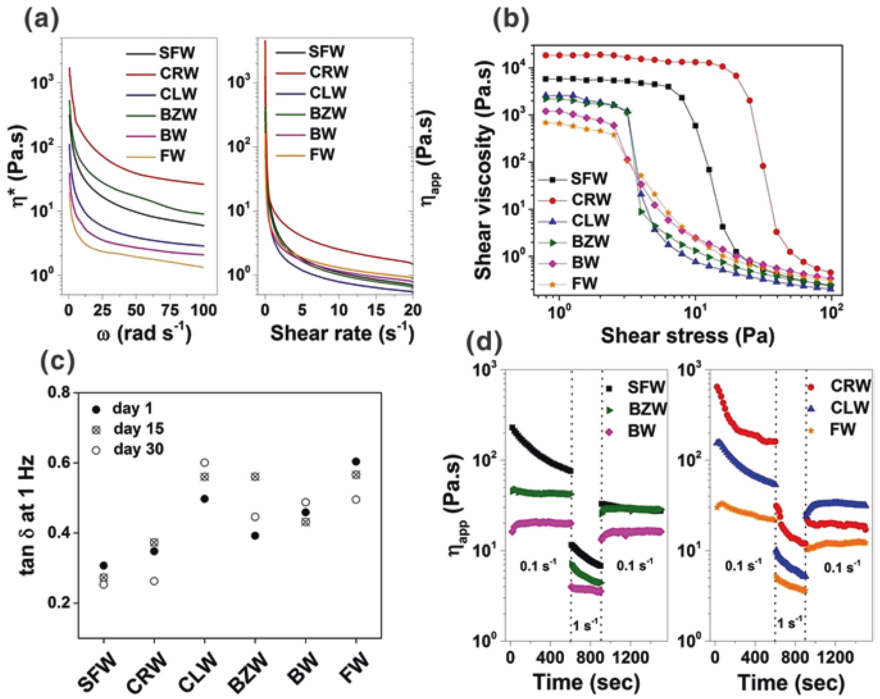

Fig. 2.5 **a** Complex viscosity (η^*) versus angular frequency (ω) and apparent viscosity (η_{app}) versus shear rate for gels made at C_g of respective waxes; **b** Results from stress sweeps for gels made at C_g of respective waxes; **c** Damping factor (tan δ) determined from oscillatory measurements done on wax gels stored for a month; and **d** Results from 3-ITT apparent viscosity (η_{app}) of samples followed as a function of time at low and high shear rates

Table 2.3 Apparent yield stress ($_{\text{app}}\tau_y$), static yield stress (τ_{sy}), and flow index (n) calculated by fitting the stress versus shear rate data to Hershel Bulkley model

Waxes	$_{\text{app}}\tau_y$ (Pa)	τ_{sy} (Pa)	n
SFW	5.951 ± 0.17	6.021 ± 0.07	0.72 ± 0.0015
CRW	6.998 ± 0.20	20.064 ± 0.11	0.56 ± 0.0033
CLW	3.069 ± 0.13	3.168 ± 0.02	0.78 ± 0.0050
BZW	3.136 ± 0.04	3.292 ± 0.03	0.75 ± 0.0018
BW	2.404 ± 0.14	2.561 ± 0.01	0.71 ± 0.0013
FW	2.207 ± 0.11	2.402 ± 0.04	0.69 ± 0.0071

Data are presented as mean ± SD

of the disruption of aggregate clusters into smaller ones, which is driven by the mechanical energy. It is also important to note that although the yield stress values of these gels are rather low, they are still appreciably high to prevent gravitational settling of the particle network that structures the gels [27] which was also confirmed from the absence of any phase separation in our samples stored for more than a month at 5 °C. Moreover, the stored samples were also periodically tested using oscillatory rheological measurements to evaluate any structure changes over 4 weeks of storage and the results (Fig. 2.5c) confirm the stability of these gels.

The thixotropic behavior is best studied by tracking the material response resulting from stepwise changes in shear rate, as the coupled effect of time and shear rate can be clearly separated in such experiments [28, 29]. Specific rheological test that is utilized to measure thixotropy is known as 3-interval thixotropy test (3-ITT) and it consists of 3 consecutive steps in control rate mode with alternating low and high shear rates [22]. The fraction of η_{app} recovered in the third step or interval gives a measure of thixotropic recovery of the material [8, 30]. The plots from 3-ITT done on organogels are shown in Fig. 2.5d and the thixotropic recoveries for the gels were as follows: SFW (43.52 %), CRW gel (15.84 %), CLW (58.64 %), BZW (67.34 %), BW (80.77 %), and FW (56.52 %). The CRW gel showed the least thixotropic recovery among the studied gels in spite of having a comparatively highest viscosity at rest as well as highest τ_{sy} and ${}_{\mathrm{app}}\tau_y$. Such behavior is usually associated with brittle gels that display high gel strength and a narrow LVR as well as yield zone. However, from the results discussed in Sect. 2.3.1 (Fig. 2.4), the CRW gel did not show a 'brittle-type' failure as confirmed from a broader yield zone which indicates that the bonding in the network of crystalline particles is more heterogeneous leading to non-uniformity in bonding strength and consequent 'ductile-type' failure [31]. This non-uniformity in the bonding strength is also evident from almost a 3-fold difference between τ_{sy} ($\approx$20.06 Pa) and ${}_{\mathrm{app}}\tau_y$ (6.99 Pa) which basically tell us that a 3 times higher force is required to initiate the flow compared to maintaining flow. The network structure in CRW can thus be assumed to be a random agglomeration of aggregated crystalline particles and the local bonding strength among the aggregates may be more stronger in certain region compared to other regions due to localized crowding of aggregates. As the gel is sheared, with time, the structure breakdowns into smaller clusters of aggregates that can contribute to the viscosity enhancement of the solvent but the restructuring of these clusters into a coherent network is avoided because the Brownian motion is overcome by shear forces. In contrast, BW and BZW gels showed a reasonable thixotropic recovery (80.77 and 67.34 %, respectively). From the microstructure studies, these two gels show spherical-type of building units which are connected together into a network by weak yet more uniform type of bonding (homogenous bonding strength) and thus, all bonds can be broken down at the same applied force (supported well by narrow yield zone seen for these samples) resulting in a flow-induced structure breakdown which is non-time dependent (linear curves in first and third intervals of 3ITT, Fig. 2.5).

2.4 Effect of Solvent Type

All the results discussed above refer to the gelation behavior of waxes in common solvent—vegetable oil-HOS. Since waxes are known to show variation in the gelling behavior based on the type of vegetable oils used for gel formation, studies were also conducted to compare the properties of these six waxes in other four other vegetable oils (rice bran oil—RBO, corn oil—CO, sunflower oil—SFO, and rapeseed oil—RSO) in addition to HOS. The fatty acid profiles determined by GC-Mass for 5 oils are shown in Table 2.4. The selected oils differed in the amount of saturated, mono unsaturated, and polyunsaturated fatty acid (SAFA, MUFA, and PUFA, respectively) levels.

The C_g values for six waxes in 5 different oils are shown in Fig. 2.6a. As shown in the graph, the C_g values for linear particle forming waxes—SFW and CLW—were low (<1 %wt) in all studied oils, while FW, BW, and CRW showed consistently higher values (≥4 %wt) except for RBO where only 1 %wt of BW was sufficient to gel the oil. The low C_g of BW in RBO can be attributed to finer crystal formation of BW (Fig. 2.6b) which is different from the large spherical crystals formed in other oils. When comparing the C_g of individual waxes in 5 different oils, it was observed that most waxes have comparatively lower C_g in vegetable oils with higher proportion of SAFA as also described in the literature [2]. There could be two possible reasons for this observation: (a) the higher amount of SAFA content (an consequently higher proportion of high melting TAGs) contributes to the strengthening of the structure and (b) the relatively lower proportion of low melting TAGs depletes the solvency effect of liquid oils forcing the formation of higher crystalline mass of wax. The latter reason can be justified based on the

Table 2.4 Fatty acids analysis of vegetable oils

Fatty acids	RBO (%)	CO (%)	SFO (%)	HOS (%)	RSO (%)
C14:0	0.34	0.02	0.08	0.04	0.05
C16:0	19.97	11.64	6.99	4.12	4.76
C16:1	0.30	0.13	0.12	0.15	0.29
C16:2	–	–	–	–	0.06
C18:0	2.14	1.81	3.37	2.91	1.58
C18:1	44.23	29.53	29.42	81.34	61.89
C18:1t	–	0.04	0.03	0.02	0.03
C18:2	29.97	54.37	58.43	9.46	19.52
C18:2t	0.032	0.14	0.28	0.02	0.04
C18:3	0.76	1.18	0.06	0.18	8.85
C20:0	1.05	0.42	0.21	0.24	0.69
C20:1	0.47	0.28	0.11	0.27	1.21
C20:2	–	0.01	–	–	0.06
C22:0	0.24	0.14	0.62	0.84	0.28
C22:1	0.03	–	–	–	0.29
C24:0	0.35	0.14	0.17	0.28	0.09
C24:1	–	–	–	–	0.13
Total SAFA	24.09	14.22	11.49	8,45	7.49
Total MUFA	45.03	29.99	29.71	81.89	63.92
Total PUFA	30.76	55.75	58.77	9.65	28.54

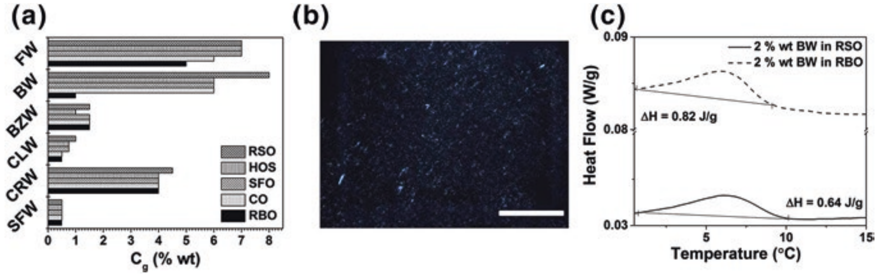

Fig. 2.6 **a** Minimum gelling concentration (C_g) of waxes in 5 different vegetable oils; **b** PLM image of RBO gelled with BW at 1 %wt, scale bar = 50 µm; and **c** cooling curves showing the crystallization of BW in oleogel prepared at 2 %wt concentration in RBO and RSO, and the mean values of the latent heat of crystallization (ΔH) are provided in the graph for comparison

results obtained from DSC measurement (Fig. 2.6c) where a comparative crystallization curves of BW in RBO and RSO are provided. BW was selected as representative example because a huge difference in C_g was observed between RBO and RSO. As seen from the curves in Fig. 2.6c, at same concentration of BW, a significantly higher latent heat of crystallization (ΔH) was obtained for crystallization of BW in RBO as compared to RSO, thus confirming the formation of higher crystalline mass of BW in RBO compared to RSO.

2.5 Conclusions

The rheological behavior of wax-based physical gels can be assumed to have characteristics of flocculated suspension (at low volume fractions of colloidal particles) as well as semi-dilute polymer solution. At a certain concentration, C_g (analogous to overlap concentration—C^* in case of semi-dilute polymer solution), a 3D network or an agglomeration of aggregated crystalline particles is created to form a viscoelastic gel which might show ‘ductile-type’ or ‘brittle-type’ deformation under applied shear, depending on the uniformity of bonding strength connecting the aggregated particles (as seen in flocculated suspension) [32]. The C_g and the rheological behavior are strongly influenced by the morphology of primary crystalline particles, as well as the subsequent aggregation of these primary particles, which in turn, depends on the chemical components present in waxes. For instance, because of the presence of a high proportion of WEs (>95 %wt), SFW forms rod-like crystalline particles which facilitates efficient gel formation at much lower crystalline mass fraction, whereas BW forms large spherical crystals because of a high proportion of low melting FAs (>95 %wt) and can form gel only at high C_g. It is important to note that these physical gels formed at respective C_g of waxes are ‘weak gels’ and most of these gels are extremely sensitive to shear showing a strong shear thinning behavior and/or weak thixotropic recovery. Waxes also show variation in C_g depending on the vegetable oil used as solvent. In general, a comparatively lower concentration of wax is required for gelling a vegetable oil that has a higher saturation levels.

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Chapter 3
Polymer-Based Oleogels Created Using Indirect Methods

Abstract Using polymers for structuring liquid oil appears promising because there are many polymers that are approved for use in foods and most of them have been well-characterized. However, since, most of the food polymers are inherently hydrophilic in nature, they are ineffective in structuring oils due to their limited dispersibility in oil. Indirect approaches such as foam and emulsion templated processes can be used to exploit structuring properties of hydrophilic polymers (with surface active properties) which cannot be dispersed directly in liquid oils. The main aim of these indirect approaches is to achieve prehydration of polymers in aqueous phase followed by selective solvent drying in order to obtain structural framework made up of dried extended polymer sheets and strands. In the current chapter, indirect approaches are discussed with respect to the preparation protocols and properties of resultant oleogels.

Keywords Polymer oleogels · Hydrophilic polymers · Proteins · Modified polysaccharides · Rheology

3.1 Introduction

Oil structuring using food-approved polymers is an emerging strategy and holds significant promise in the area of food and nutrition. Using polymers for structuring liquid oil appears promising because there are many polymers that are approved for use in foods and most of them have been well characterized. However, since most of the food polymers are inherently hydrophilic in nature, they are ineffective in structuring oils due to their limited dispersibility in oil. Ethyl cellulose, EC (a hydrophobic cellulose derivative), is the only known food polymer to gel edible oil through direct dispersion of polymer in oil. The EC oleogels are prepared by shearing the polymer dispersed in liquid oil at temperatures well above the glass transition temperature of ethyl cellulose, and the subsequent cooling results in formation of a polymer network (stabilized by physical

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interactions such as hydrogen bonding and hydrophobic interactions) that entraps the liquid oil leading to gelation [1]. However, since the processing temperatures are quite high (130–145 °C), the quality of oleogel is affected by the oxidative deterioration of oil component among other things [1]. Moreover, this approach seems to work only with EC which is a hydrophobic cellulose derivatives.

When considering hydrophilic polymers, they play an important role in providing structural framework to water-based gels, but they are quite ineffective in structuring hydrophobic oils. Functionality of polymers to form structural framework in aqueous solvent is attributed to their hydration into an extended and open conformation which result in stronger molecular interactions with the solvent [2, 3]. Thus, in order to use hydrophilic polymers for oil structuring, it is important to first prehydrate them in water phase and arrest these hydrated conformations in dehydrated form such that they can be used for physical entrapment of oils. Some food polymers such as proteins and modified polysaccharides are surface active and conformational framework can be created from water dispersions of these polymers by first promoting their adsorption to air–water or oil–water interfaces followed by stripping-off the water to obtain dried microstructures [4–6] In the current chapter, two indirect approaches (foam and emulsion-templated) for structuring liquid oil are discussed in terms of processing conditions and properties of obtained oleogels.

3.2 Foam-Templated Approach

3.2.1 Preparation of Oleogels and Microstructure Studies

Hydrophilic cellulose derivatives such as hydroxy propyl methyl cellulose, HPMC and methylcellulose, MC are synthetically prepared by substituting hydroxyl groups on cellulose backbone with methoxy and hydroxyl propyl groups. Depending on the degree of polymerization (DP) and degree of substitution (DS), different viscosity grades of HPMC and MC are commercially available. The substitution adds hydrophobic character to the molecules and thus they show amphiphilic behavior and certain degree of surface activity which imparts them the foam and emulsion stabilizing properties [3]. As previously reported, the surface active properties of HPMC was exploited to prepare aqueous foam with high overrun (high incorporation of air) which was subsequently subjected to lyophilization for stripping-off the water. The resultant dried microstructure (porous cryogel) had a reticulated cellular structure with mesh sizes in micron ranges (Fig. 3.1b).

The aqueous foam generated had an average bubble size (obtained from optical microscopy images, Fig. 3.1a) of less than 150 μm. The voids or foam cells in the porous materials were non-uniform and the dimensions were larger than the size of air bubbles in the aqueous foam; this is a characteristic microstructure of cellulose-based solid foams prepared through physical foaming [7]. The growth in the void dimension relative to the size of bubbles in aqueous foam can be explained

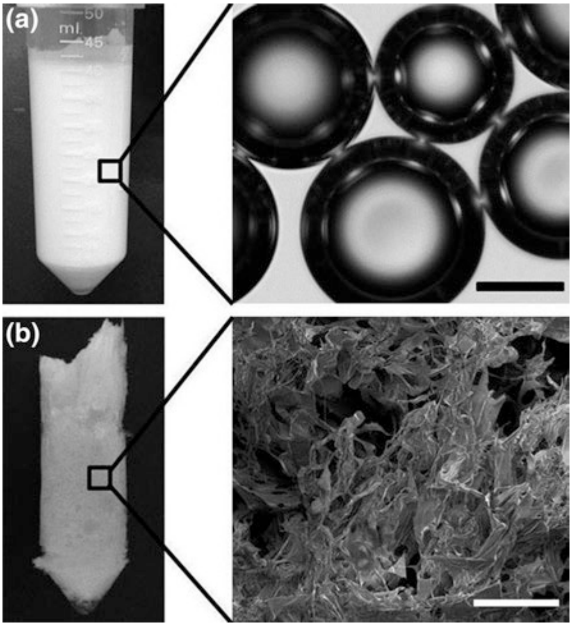

Fig. 3.1 **a** Photographs and optical light microscopy image (scale bar = 50 μm) of aqueous foam and **b** Photograph and microstructure of dried porous cryogel studied under scanning electron microscope (scale bar = 200 μm)

by the gas expansion-induced foam destabilization (Ostwald ripening and coalescence) [8] that might have occurred during the long drying time (48 h) in lyophilizer. Due to the porous structure, the cryogel showed excellent oil absorption property with a high swelling capacity (absorbing oil at 98 times its own weight within few seconds). The quick absorption of oil by the cryogel can be clearly followed from the series of pictures taken every 60 s (Fig. 3.2a). In this study, the liquid sunflower oil was stained with oil soluble dye (Nile red) for better contrast.

It is important to note here that the absorbent property of cryogel was akin to the absorbing property of a reticulated solid foam (with open cells) [9], i.e., the oil could easily flow through the entire structure and hence be quickly absorbed but not tightly bound and thus could be oozed out under minimum pressure. In order to prevent release of oil under pressure, this oil-absorbed material was sheared to uniformly disperse the polymer sheets in the oil continuous phase resulting in the formation of oil gel where the oil was physically trapped in the network of dispersed polymer sheets. The microstructure of sheared oleogel was studied using different microscopy techniques as shown in Fig. 3.2b–d. Interestingly, as shown in Fig. 3.2c, the well-formed polymer network (responsible for trapping oil into a viscoelastic gel structure) was highly birefringent. There could be two possible explanation for this behavior: firstly, the birefringence may arise due to the inherent semi-crystalline nature of cellulose derivatives and secondly, this could be a result of structural birefringence induced due to the alignment of polymer molecules at the air–water interface under freezing and subsequent drying through sublimation [10].

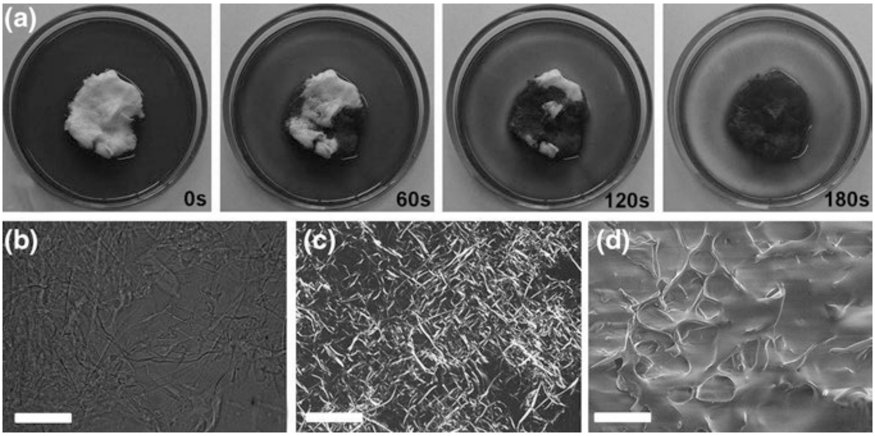

Fig. 3.2 **a** A series of photographs displaying the quick oil absorption by porous cryogel. Sunflower oil with Nile red dye was used for clear representation and images were captured every 60 s and **b** to **d** Microstructure of oleogel studied using transmission microscopy, polarized light microscopy, and cryo-SEM (scale bars = 100, 200, and 50 μm, respectively)

3.2.2 Properties of Oleogels

Four different grades of HPMC (15, 50, 100 and 4000 cps) were used to prepare cryogels. As expected, the low viscosity grade HPMC (15 and 50 cps) gave higher overrun as compared to the higher viscosity grades. On the other hand, the susceptibility of foam to drainage and disproportionation was lower for the higher viscosity grades (100 and 4000 cps). Comparative frequency curves of oleogels prepared using different viscosity grades of HPMC are showed in Fig. 3.3a. While all the samples showed 'gel-like' consistency ($\tan \delta < 1$ throughout the entire frequency range), the gel strength of oleogels increased from HPMC 15 to 4000 cps. The oleogels prepared at concentrations of 1–5 wt% HPMC 4000 cps were compared using flow tests and the plot of viscosity as a function of time (shear rate kept constant at 0.1 s^{-1}) is shown in Fig. 3.3b. The complex modulus, $G*$ (the measure of total resistance of the sample to applied deformation), plotted against oscillatory stress (Fig. 3.3c) shows that the sample has a narrow linear viscoelastic region (LVR). The progressive increase of phase angle, δ with a final value reaching close to 80°, suggests that there is a gelsol transformation when the dynamic stress is increased. Further, a prominent crossover point where G'' (loss modulus) crosses over G' (storage modulus) at an oscillatory stress of 129.7 Pa (data not shown) was seen which confirms the gelsol transformation. This results suggest that the gel is kept together by rather weak internal forces which are overcome by higher applied stress. The oleogels showed thixotropic behavior resulting in the loss of viscosity over time at constant shear rate. As shown in Fig. 3.3d, viscosity values drop from an initial ~1800 to ~800 Pa.s within 20 min even when sheared at a lower

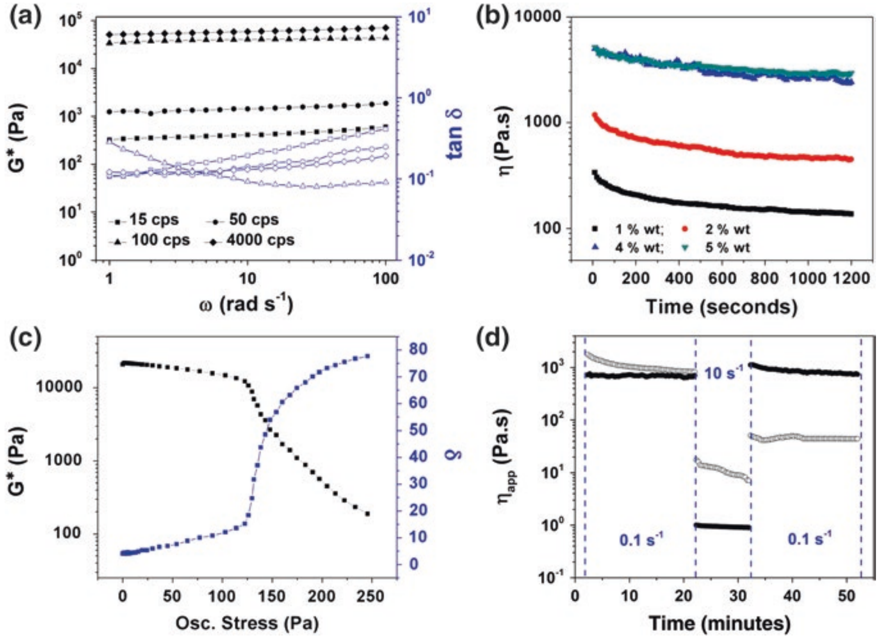

Fig. 3.3 **a** Comparative frequency sweeps done on oleogel samples prepared using 2 wt% of HPMC 15, 50, 100, and 4000 cps; **b** Viscosity curves of oleogels prepared at varying concentration of HPMC 4000 cps; **c** Amplitude (stress) sweep done on oleogel sample prepared using 2 wt% of HPMC 4000 cps and **d** Plot of apparent viscosity versus time from 3-interval thixotropy test done on oleogel prepared at 2 wt% of HPMC 4000 cps with and without palm stearin as hardstock at a concentration of 5 wt% (represented in graph as open and close symbols, respectively)

rate (0.1 s^{-1}). The system also showed a strong shear-thinning behavior with more than a 40-fold drop in viscosity from around 820 to 17 Pa.s on increasing the shear rate from 0.1 to 10 s^{-1}. As further seen from the figure, there was a negligible structure recovery when the shear rate was changed back to 0.1 s^{-1}. Thixotropic properties (with respect to the recovery of structure after shear is removed) is an important parameter which needs to be considered if the oleogels have to be used for practical applications in formulation development. Hence, in order to improve the thixotropic recovery, a small amount (5 wt%) of hardstock (palm stearin) was introduced in the oleogel. As shown in Fig. 3.3d, the incorporation of hardstock resulted in a complete structure recovery when the shear was removed.

In addition to the thixotropic properties, the tolerance of oleogels to water incorporation is also important in order to explore more broader applications. However, similar to other polymer oleogels, the incorporation of water in these oleogels resulted in a complete structure loss due to the precipitation of aggregated polymer. Thus, the applicability of HPMC oleogels is more limited and better suited for processes where oil leakage needs to be avoided at high temperatures such as baking.

3.3 Emulsion-Templated Approach

3.3.1 Background

There has been a long history of using emulsions as templates for creating dried structures containing liquid oils for food applications. Such examples include encapsulation of flavors (aromatic oils) and dried emulsions of fixed oils for reconstitution. Typically, this is accomplished by spray drying of oil-in-water emulsions to quickly evaporate the water phase and the coalescence of oil droplets into a macrophase during drying is usually prevented by either introducing a substantial amount of carrier/filler (such as maltodextrin) in the water phase [11] or by stiffening the interface through chemical, ionic, enzymatic, or thermal annealing of the adsorbed layer of surface active polymers such as proteins [12–14]. In either cases, the amount of non-oily component in the dried products is substantial and accounts for more than 30 wt%. To get a gel-like consistency, we need to ensure that the percentage of non-oil components is kept to the minimum (oil > 90 wt%). Romoscanu and Mezzenga demonstrated that protein stabilized water continuous emulsion can be converted to gels containing in excess of 95 wt% liquid oil. The process includes cross-linking of the adsorbed protein layer either thermally or chemically followed by removal of water by spray drying or under ventilation at room temperature [15]. Similarly, Gao et al. [16] also used water continuous emulsions as templates to generate oil gels by drying where the emulsions were stabilized by a complex of zein colloidal particles and stearate. Recently, in our laboratory, we found that emulsions stabilized by simple combination of food polymers could also be used as templates for generating oleogels with high oil content (>97 wt%) [5, 6]. In comparison with the previous work mentioned above, our approach requires no cross-linking or tedious colloidal particle formation steps. In the following section, several aspects of this approach are briefly discussed.

3.3.2 Preparation of Oleogels and Microstructure Studies

Emulsion-templated oleogels were prepared using a two-step process by first formulating a concentrated oil-in-water emulsion (using sunflower oil) followed by the removal of water by drying at 50–80 °C. The concentrated emulsion is stabilized by a combination of food polymers including a surface active polymer (either protein–gelatin, G or modified polysaccharides-HPMC or methylcellulose, MC) and a non-surface active polymer (complex polysaccharide-xanthan gum, X). The surface active component is responsible for stabilizing the oil–water interfaces and the non-surface active component plays a dual role of increasing the bulk viscosity of the emulsion as well as stiffening the oil–water interface resulting in improved stabilization of emulsion against physical instability (creaming) and colloidal instability (coalescence), respectively. Moreover, the incorporation of X also

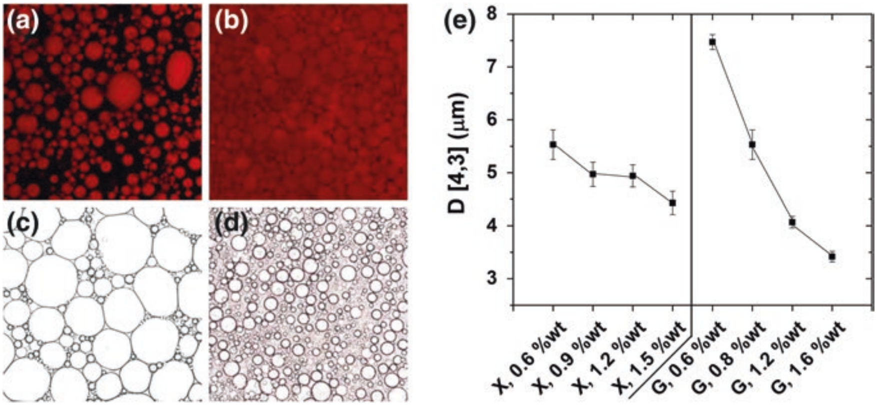

Fig. 3.4 **a** and **b** Confocal microscopy images of 60 % o/w emulsion prepared using only G and G:X as stabilizers, respectively (Image width = 300 µm); **c** and **d** Optical microscopy images of 60 % o/w emulsion prepared using only MC and MC:XG as stabilizers, respectively (Image width = 250 µm) and **e** Volume-weighted mean droplet size, D[4,3] of emulsion samples prepared at different concentration of G and X. Notice how the mean droplet size of emulsion is significantly affected by change in the G concentration, whereas the change in X concentration has comparatively less substantial effect on droplet size

results in the formation of finer and relatively mono-dispersed emulsions as evident from Fig. 3.4a–d. The mean droplet size of all emulsions prepared at different concentrations was below 10 µm and a general trend of decreasing droplet size with the increasing polymer concentrations was observed which was significant mainly in case of gelatin (Fig. 3.4e). All the emulsions prepared at different proportions of polymers had a gel-like viscoelastic behavior ($G' > G''$ at low stress values) as confirmed from oscillatory measurements (data not shown).

The emulsion samples prepared at different concentrations of polymers were subjected to water removal through drying at 50–80 °C for several hours. The time required for complete drying of emulsion was followed by weighing of samples at certain time intervals, and it was found that drying time ranged from 32 h at 80 °C to 72 h at 50 °C. Exposure of oils (rich in unsaturated fatty acids) to elevated temperatures for such lengthy time is expected to result in deterioration of the quality of oils (i.e., oxidative degradation). To confirm the extent of oxidative deterioration, the samples dried at different temperatures were subjected to analytical tests and several parameters such as peroxide value (PV), p-anisidine value (pAV), and total oxidation value ($\text{TOTOX} = 2 \times \text{PV} + \text{pAV}$). It was found that exposure to high temperature (80 °C) for shorter time showed more deterioration than exposure to relatively lower temperatures (50 and 60 °C) for a longer time. The dried samples did not show any rancidity but based on the peroxide values, they could be considered to be in a high oxidation state and most susceptible to undergo oxidation over time storage. Few options which could be used to tackle this issues include changing the drying technique to minimize oil deterioration (e.g., spray drying) and incorporation of antioxidants.

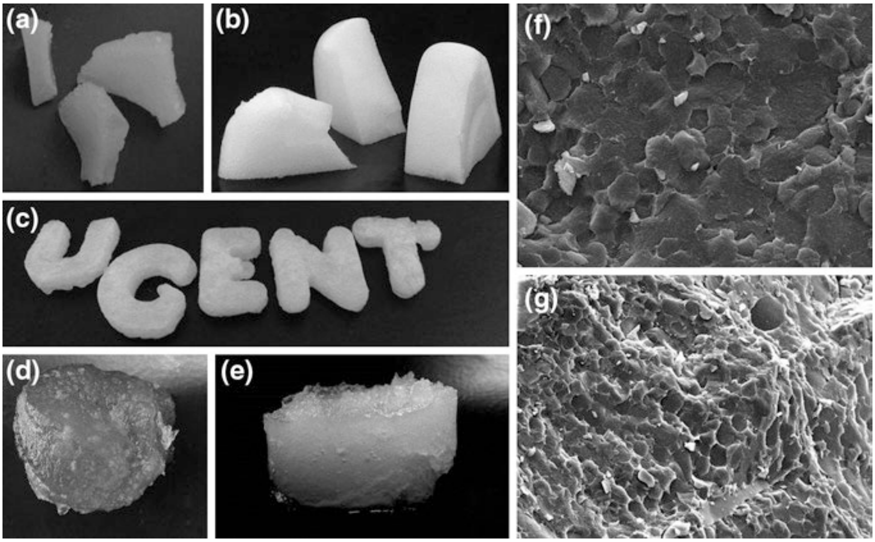

Fig. 3.5 **a** and **b** Dried solids obtained by oven drying of emulsions stabilized by a combination of G:X and MC:X, respectively; **c** Emulsions dried in molds to obtain dried solids in predetermined shapes; **d** and **e** Oleogels prepared by shearing the dried solids of emulsions stabilized by a combination of G:X and MC:X, respectively, and **f** and **g** Representative cryo-SEM images showing the microstructure of dried solid and oleogel, respectively (image widths = 100 μm and 150 μm, respectively). *Note* The dried samples consisted of more than 97 wt% liquid oil

The dried products obtained after water removal are shown in Fig. 3.5a, b, and the drying of the emulsion was also carried out in molds to obtain dried products with predetermined shapes (Fig. 3.5c). Moreover, the dried products could also be transformed into oleogels by simple shearing (Fig. 3.5d, e). The microstructure of dried solids and sheared oleogels was as studied using cryo-SEM (Fig. 3.4f, g, respectively). Due to the presence of stiffened interfaces, the removal of water did not lead to coalescence of oil droplets resulting in interesting microstructure where the oil droplets are seen packed together without any significant internal contacts. Moreover, the microstructure of the sample was retained even after shearing as shown in Fig. 3.5f where clusters of packed droplets were seen scattered in the oil continuous phase. This explains why there was no oiling off in the oleogel samples.

3.3.3 Properties of Oleogels

To characterize the properties of oleogels, a range of oscillatory (amplitude and frequency sweeps) and flow tests were conducted. As shown in Fig. 3.6a, the sample displayed gel-like viscoelastic behavior (G' higher than G'' by over a decade)

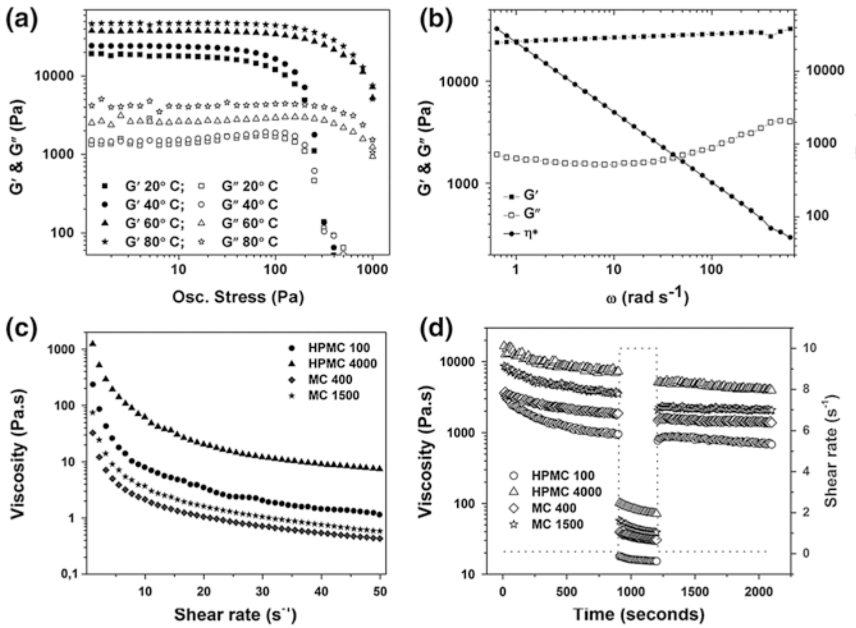

Fig. 3.6 **a** and **b** Plots from oscillatory amplitude sweeps and frequency sweep done on G:X oleogel, the complex viscosity in **b** is plotted as line + symbol; **c** and **d** Viscosity and 3-ITT curves for oleogels prepared using HPMC (100 and 4000 cps) and MC (400 and 1500 cps) along with xanthan gum, the shear rate in **d** is plotted as *dashed line*

at all studied temperatures. Interestingly, with increasing temperatures, the gel strength was seen to increase as evidenced from higher moduli as well as critical stress values. From the plot of frequency sweep (Fig. 3.6b), the strong gel strength of oleogel was evident based on following observations: (a) the G' of more than 11,000 Pa that was higher than G'' by more than a decade at all frequency values; (b) the G' was independent of the frequency as indicated by a more or less straight line, and (c) the complex viscosity ($\eta^* = G^*/\omega$) showed a proportional decrease with the increase in the frequency [17–19]. The oleogels also showed a prominent shear-thinning behavior (pseudoplastic behavior) with more than 100-fold decrease in apparent viscosities at studied shear rate ranges (Fig. 3.6c). The data from flow test (shear stress versus shear rate) were also fitted to nonlinear model (Hershel Bulkley model) and a yield stress ranging from 20 to 140 Pa was obtained for gels prepared using different grades of cellulose derivatives. And as expected, the values for flow index (n) for all these samples were well below unity further confirming the pseudoplastic flow behavior of these samples. The thixotropic behavior of these oleogels studied using 3-ITT in rotation (rot-rot-rot) is shown in Fig. 3.6d. All samples showed a drop in the viscosity over time at constant shear rate suggesting that the material response depends not only on the applied rate of shear but also on the ‘time for which the fluid has been sheared.’

The structure recovery at rest (third interval) was calculated for each sample by taking the viscosity value at the end of interval 1 as 100 %. The percentage of recovery for all the oleogel samples was in the range of 70–90 % indicating a good structure recovery at rest unlike foam-templated oleogels which showed very poor structure recovery. This difference in thixotropic behavior can be attributed to the microstructure of emulsion-templated oleogels. It could be assumed that at rest, the clusters of tightly packed droplets (that were aligned in the direction of flow at higher shear rate) return back to a more random distribution leading to an increase in the dissipation of energy or resistance to flow. Whereas in case of oleogel prepared using foam-templated approach, the network of polymer sheets does not reorganize on removal of shear. It is also important to note that in amplitude sweeps, unlike emulsion-templated oleogel, the foam-templated oleogel does show a crossover point indicating a complete liquification of sample.

3.4 Conclusions

Hydrophilic polymers such as proteins and polysaccharides have long been used for structuring water gels. The structuring functionality of polymers is dependent on their hydration in water leading to their extended conformations in the solvent which assist in the formation of continuous structural framework that is able to physically trap a large amount of water. Since edible oils are hydrophobic in nature, these polymers show poor dispersibility in these solvent and consequently, it is not possible to use hydrophilic polymers to structure liquid oils. However, it is interesting to note that some of these polymers have amphiphilic characteristics (display surface activity) and are known to have some affinity for hydrophobic oils. In the current chapter, it was demonstrated that indirect approaches could be used to first hydrate them in water followed by their adsorption on air–water and oil–water interfaces. These stabilized colloids are then used as templates to create structured oil systems. The microstructure studies of these systems reveal that structuring of oil is achieved by sheets of polymers forming a network in oil continuous medium (in case of foam-templated oleogels) or by tightly packed oil droplets dispersed in network of surface adsorbed polymers. The advantage of these approaches includes a relatively lower temperature processing, structuring at low polymer concentration, and flexibility of using other polymers that show surface activity.

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Chapter 4
Inorganic Particle-Based Oleogels

Abstract Fumed silica has a complex microstructure comprising of micron-sized agglomerates of submicron aggregates of nanosized primary particles. Due to this complex microstructure and interesting surface chemistry, fumed silica is capable of forming oleogels through the formation of a continuous 3D network stabilized by hydrogen bonding among particles. These oleogels can be further combined with weak water gels to create a relatively unexplored class of colloids called bigels. The microstructure and rheological properties of fumed silica-based oleogels and bigels are described in details in this chapter.

Keywords Fumed silica · Inorganic particles · Bigels · Oleogels · Arrested demixing · Thixotropy

4.1 Introduction

Inorganic particles such as clay have long been used for structuring and rheology modification of water-based systems. Depending on the concentration of clay, different type of structured systems, ranging from dilute suspension to thixotropic gels and pastes, can be obtained. For structuring non-aqueous solvents, organophilic clay (made by association of long-chain organic compounds) is used as structuring agent [1]. Hydrophilic inorganic particles such as hydrophilic fumed silica have also been studied for their rheology modifying effects on organic solvents. Fumed silica is prepared using flame hydrolysis process which results in a complex agglomerated structure with large specific surface area [2]. The hydrophilic characteristics result from the presence of hydroxyl groups on the surface of particles. When dispersed in nonpolar solvents, the aggregates of silica particles can interact together (via H-bonding of surface hydroxyl groups) to form larger structures called flocs that can further organize into a network, resulting in a large increase in the viscosity and gel-like viscoelastic behavior [3]. In a triglyceride solvent (liquid edible oil), the viscosifying properties of fumed silica is well known and is attributed to a reversible, three-dimensional lattice structure which

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breaks down under shear (shaking or stirring) but builds up again at rest, contributing to the thixotropic characteristics of fumed silica dispersions [2]. Recently, it was found that fumed silica could be used as gelator to create viscoelastic gels of sunflower oil at concentrations of 10 and 15 wt%. Further, this structured oil systems could be used along with water gels for fabricating unusual colloidal systems called bigels [4]. In the current chapter, the properties and microstructure of fumed silica-based oleogels and bigels are briefly discussed.

4.2 Fumed Silica-Based Oleogels

4.2.1 Complex Structure of Fumed Silica

Since flame hydrolysis process is used for the preparation of fumed silica, the resultant microstructure of final product is quite complex and can be viewed at three different length scales (Fig. 4.1a–c), comprising of primary particles (size range = 5–50 nm) fused into stable fractal aggregates (size range = 100–500 nm) which further grow into micron-size agglomerates stabilized by hydrogen bonding and electrostatic interactions [5, 6]. The aggregates have an open structure (3D

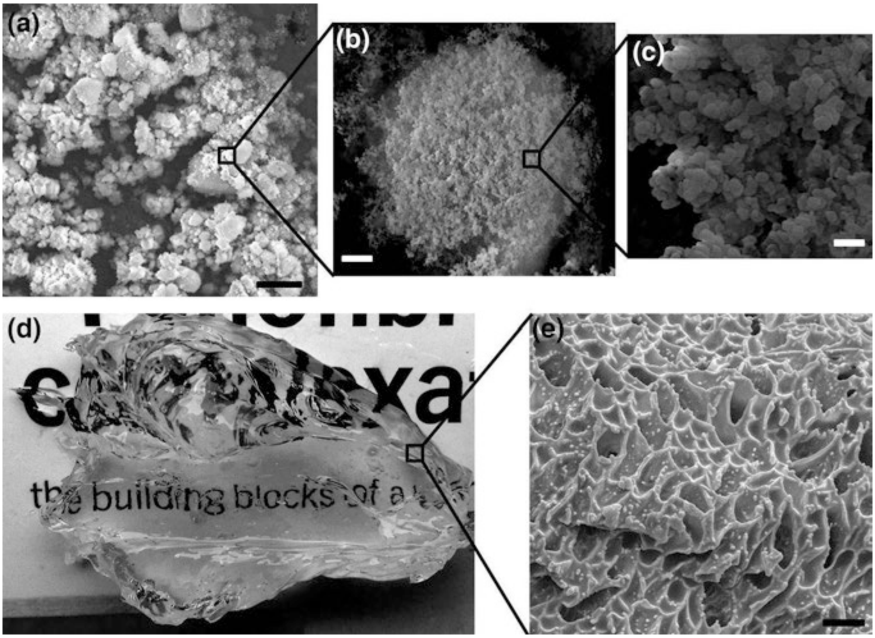

Fig. 4.1 **a**–**c** Cryo-SEM images showing different levels of fumed silica (scale bars = 100, 2 and 0.5 µm, respectively) and **d** and **e** Photograph and microstructure of silica-based oleogel studied under cryo-SEM (scale bar = 2 µm)

fractal dimension, $D_{f,\,3} \approx 2.0$), while the agglomerates are much more compact ($D_{f,\,3} \approx 2.5$) [7]. The fractal dimension can be used as a measure of the degree of openness, or compactness, of the aggregates. The open chainlike aggregates have a dimension of around 1, whereas the fractal dimension of 3 is indicative of compact aggregates [7]. As a result of this complex aggregation structure, fumed silica exhibits high specific surface area (SSA). Different grades of fumed silica with varying SSA values are commercially available. In this work, different grades of Aerosil® fumed silica—A150, A200, A300, and A380 with average SSA of 150, 200, 300, and 380 m^2/g, respectively, were used to gel sunflower oil. In general, the higher the SSA, the greater is the degree of agglomeration. The agglomerates are held together by weak forces including H-bonding and van der Waals forces. When fumed silica is dispersed in solvents under high shear, the agglomerates can be broken down into aggregates of primary particles. Depending on the polarity of the solvent, the aggregates can reorganize into continuous network with open structure which can provide a structural framework for physical trapping of the solvent.

4.2.2 Preparation and Characterization of Oleogels

The fluffy powder (tamped density = 50 g/l approximately) of Aerosil was dispersed in liquid sunflower oil at room temperature using high-energy-dispersing unit (Ultraturrax® at 11,000 rpm). Use of high-energy shearing is necessary to ensure wetting and uniform dispersion of fumed silica in the liquid oil. The dispersion time used in the study was less than 5 min to prevent any temperature build up in the system which could negatively influence the structuring properties of fumed silica [2].

Hydrogen bonding between the unsubstituted hydroxyl groups on particle surface is responsible for creating three-dimensional network of aggregated particles in organic solvents [8]. Accordingly, the hydrophilic grades of fumed silica showed better gelation of oil compared to the hydrophobic grade-A972. The surface chemistry of fumed silica is attributed to the surface silanol groups (Si–OH) some of which may be functionalized to obtain hydrophobic fumed silica. In case of A972, the surface treatment is carried out with dimethyl dichloro silane (DDS).

The data from stress sweeps done on oleogels prepared at constant concentration (15 wt%) of different Aerosil grades are shown in Fig. 4.2a. All the oleogels prepared using hydrophilic fumed silica displayed strong gel properties with elastic modulus (G') being higher than viscous modulus (G'') by a factor of 10 at low stress values. Among hydrophilic fumed silica, the A200 oleogel showed best rheological properties as evident from high moduli values, broader linear response region and high oscillatory yield point. On the other hand, A972 oleogel had a weak structure (with moduli values below 200 Pa) that showed yielding at stress of less than 10 Pa. On comparing the flow properties (Fig. 4.2b), the contrasting behavior of gels was evident with A972 oleogel showing a distinct time-dependent decrease in viscosity at constant shear rate (thixotropy) whereas, oleogels made from some hydrophilic fumed silica (A150, A200, and A300)

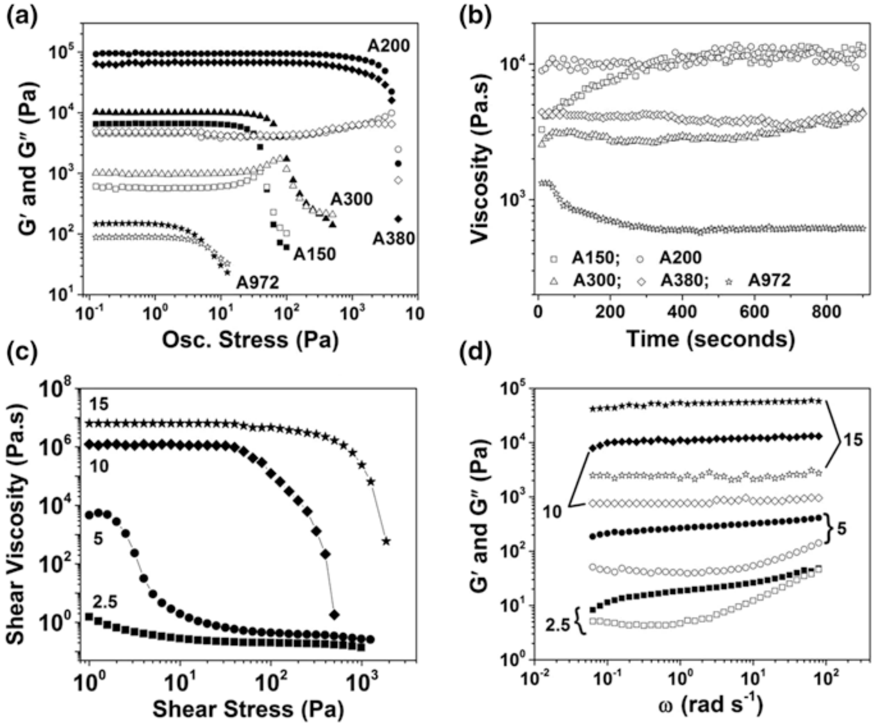

Fig. 4.2 **a** Oscillatory amplitude sweeps of oleogels prepared at 15 wt% of A150, A200, A300, A380, and A972, the filled and open symbols represent G′ and G″, respectively; **b** Viscosity plotted as a function of time at constant shear rate (0.1 s^{-1}) for oleogels prepared using 15 wt% of A150, A200, A300, A380, and A972; **c** and **d** Comparative curves from stress ramp and frequency sweeps for sunflower oil dispersions containing 2.5, 5, 10, and 15 wt% of A200. In Fig. 4.2d, the filled and open symbols represent *G′* and *G″*, respectively

showed a time-dependent increase in viscosity (negative thixotropy or rheopexy). Such increase in viscosity with time at constant shear rate has been documented in past is believed to be caused by the clustering of silica particles [9–11].

To study the influence of concentration, oleogels were also prepared at 2.5, 5, 10 and 15 wt% of A200. At low concentrations of fumed silica (2.5 and 5 wt%), the dispersions behaved like fluid viscous sols that flowed under the influence of gravity (yield stress <2.5 Pa). While, concentration of 10 and 15 wt% gave strong gels that displayed a significantly higher yield stress (Fig. 4.2c) and less frequency dependent oscillatory shear response (Fig. 4.2d).

The microstructure of A200 oleogel was studied using cryo-SEM after de-oiling the gel sample beforehand. The microstructure studies revealed the intricate network of silica particles (Fig. 4.1d) which is responsible for physical trapping of liquid oil in gel-like structure. The structuring functionality of fumed silica dependent on firstly on the uniform dispersion of fumed silica in the solvent where the micron-size agglomerates (Fig. 4.1b) are broken down into smaller submicron aggregates and distributed homogeneously in the continuous solvent phase followed by re-organization of aggregates to form open network structure that is capable of arresting the mobile solvent molecules. The gel was optically clear and showed Tyndall scattering (results published elsewhere) [4] thereby, confirming that the structuring units (aggregates of primary particles) were considerably smaller that the lower wavelength of visible light (i.e. 400 nm). It is also interesting to note here that the oleogel turn slightly hazy on storage (after few weeks) accompanied with the increase in gel hardness thus, suggesting a time-dependent evolution and strengthening of the network.

4.3 Fumed Silica-Based Bigels

4.3.1 Preparation and Microstructure of Bigels

As mentioned in previous chapters, one of the critical considerations for applicability of oleogels in real food systems is their ability to tolerate the presence of water. Incorporation of water in the oleogel resulted in loss of consistency because of the partitioning of hydrophilic silica particles in the water phase. In order to maintain the consistency, water phase structured with hydrocolloids (locust bean gum, LBG, and carrageenan, Car) was combined with oleogel to create complex colloidal system called bigels (Fig. 4.3a). Bigels are bicontinuous colloids which are a relatively unexplored class of soft matter systems [12]. They have generated recent interest because they display interesting rheological properties owing to their complex microstructure where the two phases form interpenetrating, percolating network [13, 14]. LBG and Car are both non-gelling polymers, however, when combined together, they show synergistic interactions, resulting in gel formation. As reported by our group previously, a synergistic interaction of LBG:Car results in the formation of thermoreversible, weakly structured gel or ‘weak gel’ [15, 16]. Bigels were prepared by mixing oleogel (15 wt% A150) with water gel (heated to 60 °C) at varying proportions (O:W ratio of 9:1, 8:2, 7:3 and 6:4) using mild stirring. The microstructure of bigel was studied using a range of microscopy techniques including optical, confocal and cryo-SEM along with energy dispersive x-ray spectroscopy (EDS). Figure 4.3b clearly displays the discontinuous distribution of water phase (unstained black areas) in the stained oil phase (stained bright and dark areas). The distribution pattern of two phases is also visible in the cryo-SEM image taken on a freeze fractured sample (Fig. 4.3c). The removal of water (through sublimation) left a porous mesh of polymer matrix interspersed between the discontinuous oil–solid phase. This focused area of the sample was also subjected EDS analysis and the elemental map of Si that was created based on the spectral analysis is shown in Fig. 4.3d. As expected, the elemental map indicates that silica particles preferred to partition from oil phase into the water phase owing to their hydrophilic nature. However, even with this partition, the overall rheology of bigel was significantly better than its components (i.e. oleogel and water gel). A surface adsorption-based interaction of polymer chains with silica

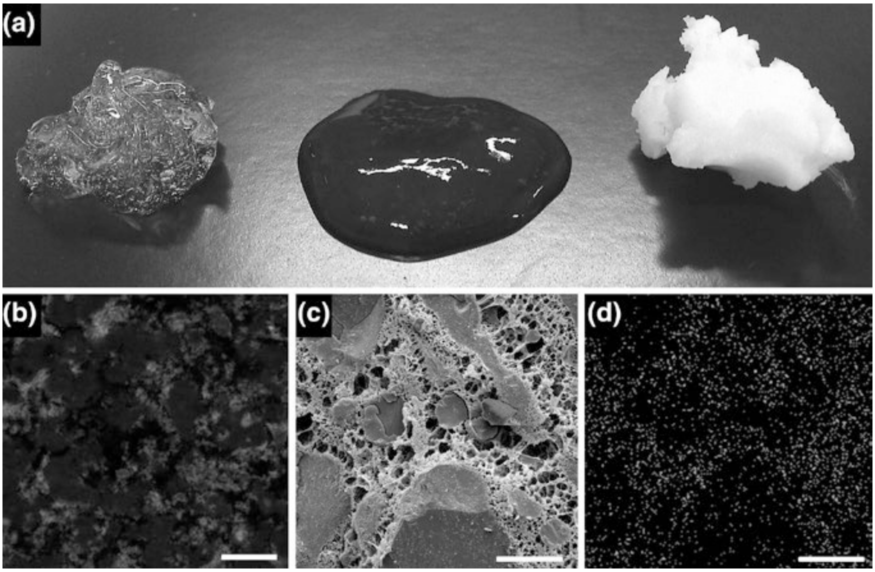

Fig. 4.3 **a** From *left* to *right*: Photograph of 15 wt% A150 oleogel, water gel (1 wt% LBG:Car, 1:1), and bigel prepared at O:W ratio of 8:2 ratio; **b** Confocal microscopy image of bigel prepared at O:W ratio of 8:2, the stained bright and dark areas correspond to oil phase, and the unstained *black areas* represent water phase (scale bars = 25 μm); and **c** and **d** Cryo-SEM image of bigel prepared at O:W ratio of 6:4 imaged after sublimation of water and the corresponding elemental map showing the distribution of silicon (shown as *bright dots*) in the bigel sample as recorded using EDS (scale bars = 10 μm)

particles in the water phase is possible [9, 17] and this could be considered responsible for the overall enhancement of the rheology of bigels. Further, the influence of varying O:W proportions on microstructure of bigels can be clearly seen in Fig. 4.4. Samples were prepared using structured water phase doped with staining dye in order to understand the distribution of phases in different bigel samples. As the proportion of water phase is increased, the microstructure shows a defined change from a one-component percolation network to a double percolation or two component percolation network [17].

4.3.2 Properties of Bigels

The data from amplitude stress sweeps done on bigel samples are shown in Fig. 4.5a, and the bigel samples showed higher gel strengths than the oleogel as indicated by comparatively higher G' values, higher G'/G'' ratios as well as higher values of oscillatory yield stresses (compared to the data on oleogel shown in Fig. 4.2a). The shape of curves indicates that the rheological response of bigels is highly dominated by the oleogel component at all the studied O:W ratios. However, since all the bigels

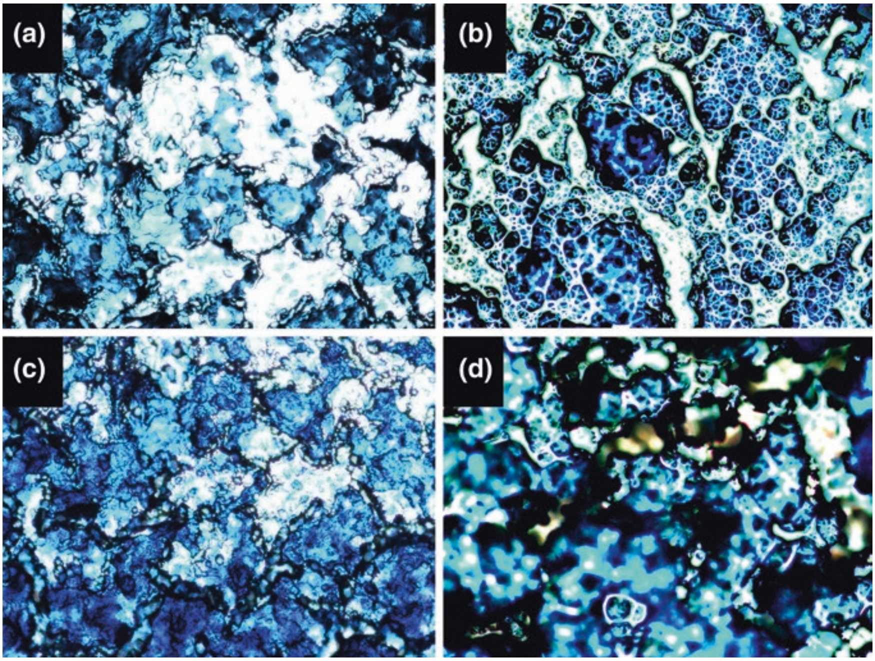

Fig. 4.4 **a**–**d** Optical microscopy images of bigel samples prepared at O:W ratios of 9:1, 8:2, 7:3 and 6:4, respectively. The water phase doped with water-soluble dye (fast *green* FCF) was used for bigel preparation. (*Image width* 500 μm)

showed a higher gel strength compared to oleogel, it can be speculated that the formation of semi-continuous interpenetrating phases of oil and water in bigels contributes to the overall rheology of the samples. The synergistic effect on rheology of bigels could be explained from the interpenetrating network of oil and water phases. It has recently been understood that similar to the colloidal gel formation seen in case of short-ranged attractive colloids (SRAC), arrested demixing of binary colloidal mixtures also results in ramified space-spanning structures (bigels) due to an interplay of phase separation and arrest. Moreover, it was recently confirmed in the work of Di Michele et al. that a bigel is capable of bearing significantly higher stress compared to a one-component gel [12]. As proved using cluster analysis, the enhancement in the rheological properties of two component gel is due to the rearrangement of particles under deformation into multiple smaller clusters instead of a single compact cluster seen in one-component gels [12]. In addition, a clear influence of increasing the oleogel proportion on the enhancement of gel strength was also observed as indicated by increase in the critical stress values (highlighted with an arrow in Fig. 4.5a).

Other rheological properties of bigels were also studied using flow measurements, 3-interval thixotropy test (3-ITT), and oscillatory temperature ramps. The flow behavior shown in Fig. 4.5b suggests strong shear thinning (pseudoplastic flow) for one-component gels (water gel and oleogel) as well as bigels prepared

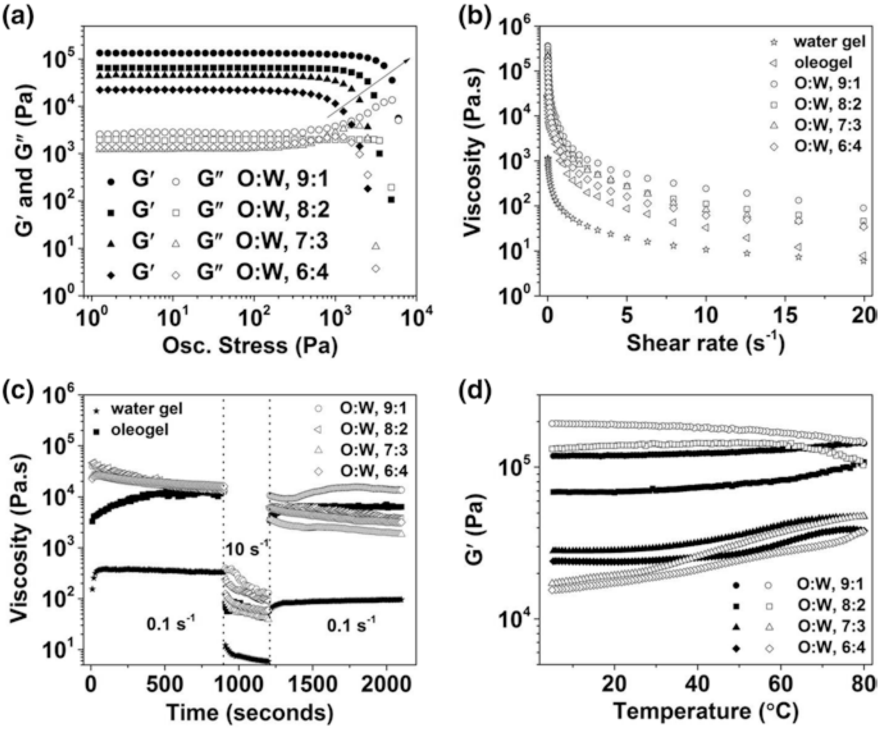

Fig. 4.5 **a** Data from amplitude stress sweeps done on bigels prepared at different O:W ratios, and the increase in the gel strength of the bigel with increasing proportion of oleogel is indicated on the graph by an arrow; **b** Viscosity curves of water gel, oleogel, and bigels prepared at different O:W ratios; **c** Plots from 3 interval thixotropy test done on water gel, oleogel, and bigels prepared at different O:W ratios; and **d** G′ measured as a function of temperature for bigels prepared at different O:W ratios, and filled and open symbols represent heating and cooling steps, respectively. Adapted from Patel et al. [4]

at varying O:W ratios. It is also interesting to note that the viscosity values at rest showed a decrease with the increase in the water proportion in bigels.

The effect of time and shear history on the viscosity of bigels was studied to understand the structure recovery properties. As seen from Fig. 4.5c and Table 4.1, water gel and oleogel showed distinct difference when subjected to 3-ITT, while water gel showed no apparent change in the viscosity values over time in the first interval and the viscosity of oleogel increased with time. This behavior of oleogel is indicative of rheopexy or negative thixotropy as explained previously in Sect. 4.2.2. In addition, in the 3rd interval, the structure recovery of water gel was quite low (<30 %), whereas oleogel showed a complete structure recovery. The bigels on the other hand showed properties which were different form either of one-component gels. For instance, in the first interval, all bigel samples showed thixotropic behavior (decrease in viscosity values with time at constant shear rate) followed by much lower structure recovery (<20 %) in the third interval.

Table 4.1 Data from 3 interval thixotropy test done on water gel, oleogel, and bigels

Samples	Viscosity at the start of interval 1 (η) in Pa.s$_1$	Viscosity at the end of interval 1 in Pa.s	Peak viscosity in interval 3 (η_3) in Pa.s	Structure recovery (%) $(\eta_3/\eta_1) \times 100$
Water gel	332 ± 21	359 ± 39	97 ± 1.9	29.36 ± 1.3
Organogel	3599 ± 338	12753 ± 1275	5163 ± 188	>100
Bigel (O:W, 9:1)	42035 ± 926	12375 ± 1201	5705 ± 161	13.56 ± 0.9
Bigel (O:W, 8:2)	31945 ± 816	14130 ± 1371	5298 ± 43	19.98 ± 1.9
Bigel (O:W, 7:3)	25250 ± 1640	13345 ± 1096	1766 ± 81	6.96 ± 1.2
Bigel (O:W, 6:4)	25065 ± 120	15785 ± 247	3960 ± 29	15.10 ± 2.1

On comparing the temperature behavior (Fig. 4.5d), all bigels displayed an increase in the gel strength during the heating step similar to oleogel (data not shown). The increase in the gel strength with the rise in temperature for silica gels in apolar solvents has been explained by the increase in the fractal dimension of the aggregates resulting in compact packing which consequently leads to stronger H-bonding due to the closeness of packed particles [18]. During the cooling step, two different kind of behaviors were observed. In case of samples with relatively higher proportion of oleogel (O:W = 9:1 and 8:2), the final values of the G' after the cooling step were higher than the initial values, whereas for the other two samples, the final values were much lower than the initial values. The plausible explanation for this observation is that the increased proportion of water phase leads to the partitioning of a greater proportion of silica particles in the water phase which affects the restructuring of silica particles and the consequent strengthening of particle network on cooling.

4.4 Conclusions

In summary, it was demonstrated that fumed silica can be used to generate oleogels when a sufficiently high concentration is used ($\geq$10 wt%). Owing to the complexity of agglomerated structure of fumed silica, the dispersion needs to be carried out under high shear in order to first break apart the micron-size agglomerates into submicron aggregates of primary particles. The uniformly dispersed aggregates can then reorganize into open network structure (mediated via H-bonding) to provide structural framework for gel formation. Since the dimensions of structuring units are well below the wavelength of visible light, the obtained oleogel is optically clear. Most interesting aspect of this oleogels is the possibility of creating novel bigels when they are combined with water gel as certain proportions. The bigel formation occurs due to arrested demixing of two structured phases resulting in semi-continuous interpenetrating network of oil and water phases. Due to this interesting microstructure, the rheological properties of bigels are completely different from either of the individual component gels.

For instance, though the bigels show a comparatively higher gel strength, the structure recovery behavior was much weaker than the oleogel. Moreover, since the rheological properties are significantly influenced by the proportion of phases, new opportunities of tuning the bigel properties can be envisaged.

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Chapter 5
Potential Food Applications of Oleogels

Abstract Oleogelation strategies aimed at creating soft matter structures with the functionality of fats, but with nutritional profile of liquid oils (i.e., low in saturated fats and high in unsaturated fats), currently represent an important area of research that is highly relevant from product development point of view. Some recently published results exploring the potential food applications of oleogel systems are briefly reviewed.

Keywords Edible oleogels · Spreads · Chocolate pastes · Full-fat shortenings · Emulsified shortenings · Wax-based oleogels · Polymer oleogels

5.1 Introduction

Earlier studies in the area of oleogelation were mainly focused on the fundamental understanding of the structuring principles, but in recent years, more reports on exploring functionality of oleogels for potential applications in actual food formulations have been published. Some notable examples are as follows:

(a) Use of ethyl cellulose (EC) oleogels to replace a part of beef fat in frankfurters: Both the hardness and chewiness of frankfurters made with gelled oil were found to be not significantly different from beef fat control. The comparative functionality of EC oleogels to beef fat was attributed to the ability of oleogel to match the fat globule size distribution (in specific size range) [1]. (b) Heat-resistant chocolate made by incorporating EC: Although not used as oleogel per se, the approach does exploit the oil binding and sugar network enhancing properties of EC to produce heat-resistant chocolates [2]. EC was introduced in molten chocolate as ethanolic solution followed by evaporation of solvent to obtain ethanol-free chocolates [3]. (c) Wax-based oleogel for saturated fat replacement in ice cream formulation: Encouraging results were obtained with rice bran wax oleogel where it was observed that oleogel could induce fat droplet network formation provided that a high concentration of oleogel is used along with emulsifier such as glycerol

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Fig. 5.1 From *left* to *right*: oleogel-based spread prepared without emulsifiers and chocolate paste where oleogel was used for complete and partial replacement of oil binder and palm oil, respectively, and 4/4 sponge cakes prepared using oleogel as shortening

monooleate [4]. (d) Wax-based oleogels of hazel nut oil in preparation of cookies: The functionality of wax oleogels was compared to commercial bakery shortening (CBS) for preparation of cookies. Oleogel cookies showed comparable texture and stability properties to CBS cookies which were well accepted by consumers [5]. (e) Wax-based oleogel for margarine production: On comparing the margarine production from oleogels made using sunflower wax (SFW), rice bran wax (RBW), and candelilla wax (CW), it was observed that the gelation behavior of waxes cannot be directly correlated to stable margarine formation. For instance, CW and RBW formed firm oleogels, but in margarine formulation, CW showed phase separation, while RBW could not provide desired firmness. SFW was found to be the most suitable structurants of the three studied waxes [6].

In addition to above-mentioned examples, recent results on potential food application of wax- and polymer-based oleogels (Fig. 5.1) have been published from our laboratory [7, 8]. This chapter gives a brief account of these potential applications.

5.2 Oleogel-Based Spreads with Varying Water Levels

The total content of fat in spreads varies from 80 %wt for full-fat spreads (regular margarines) to 60 %wt for reduced-fat and 40 %wt for low-fat spreads. As the fat content is lowered, the emulsification and stabilization become much more challenging because of two main factors: (a) enhanced viscosity of the emulsion (resulting from the increase in the phase volume of dispersed water phase) that increases the challenge of achieving finer droplet sizes and (b) decrease in the crystalline phase (due to the decrease in the fat content) which increases the possibility of aggregation and coalescence of water droplets [9]. Thus, the choice of emulsifier as well as the selection of hard stock becomes more critical in formulating reduced- and low-fat spreads. In this work, shellac wax-based oleogels were successfully used as fat phase to generate emulsifier-free spreads (at water content of 20–60 %wt) without the use of hard stock. Waxes are chemically composed of several components including nonpolar wax esters and long-chain hydrocarbons as well as polar components such as fatty alcohols. Among these components, linear molecules such as wax esters and hydrocarbons can form crystals that prefer one-dimensional growth (needle-like morphology) and thus can connect together to form a three-dimensional network at much lower crystalline mass fraction compared to high-melting triacylglycerols which form plate-like crystals. On the other hand, components like fatty alcohols can act as dispersing agents due to their amphiphilic characteristics. Shellac wax (SW) is purified waxy fraction of crude shellac secretion from lac insect, *Laccifer Lacca,* and chemically, it is mainly composed of wax esters (approx. 60 %wt) and fatty alcohols (≈35 %wt) [10] Because of high proportions of wax esters and fatty alcohols (majorly 1-octacosanol) [11], SW is very efficient at gelling liquid oils as well as stabilizing oil continuous emulsions [12, 13].

Oil continuous emulsions were prepared by emulsifying melted SW oleogels with varying amount of water followed by cooling to room temperature. Emulsions with water content of 20–60 %wt were obtained while keeping concentration of SW constant at 5 %wt of total emulsion. The presence of amphiphilic fatty alcohols ensures the initial dispersion of water into fine droplets, and with the further drop in temperature, crystallization occurs in bulk as well as at the water–oil interfaces contributing to the stability of emulsion. As seen from PLM and cryo-SEM images (Fig. 5.2a, b), the stabilization of emulsion was a result of bulk

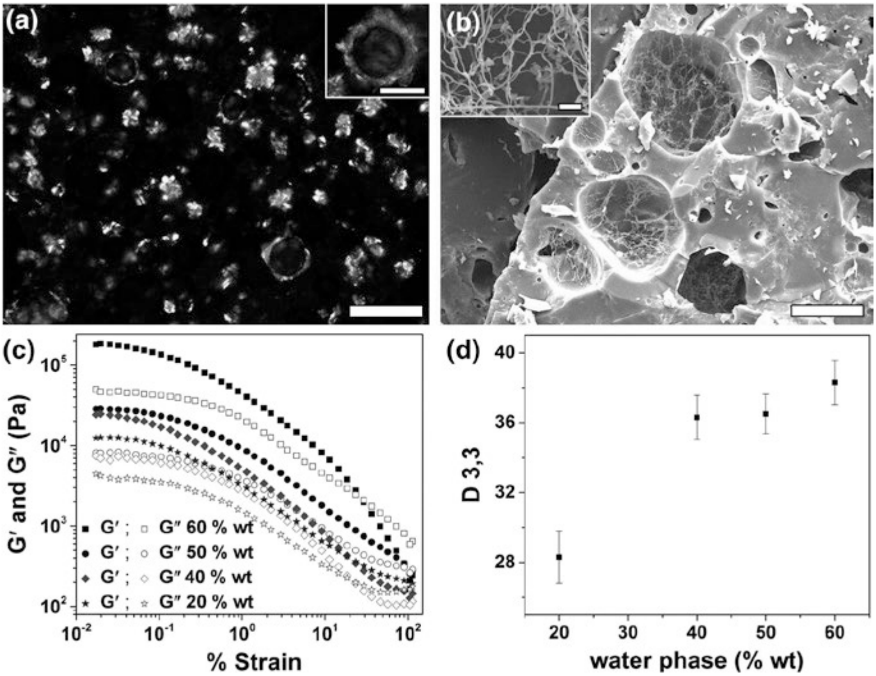

Fig. 5.2 **a** PLM image of emulsion (scale bar = 50 μm), *inset*: magnified image of water droplet showing the presence of crystal at droplet interface (scale bar = 25 μm); **b** Cryo-SEM image of freeze-fractured emulsion sample (scale bar = 25 μm), inset: magnified image of the network of fine crystallites left after the removal of dispersed water through sublimation (scale bar = 200 nm); (**c**, **d**) Comparative rheology and mean droplet sizes, respectively, of emulsion formed at water phase levels of 20–60 %wt). Reprinted from Patel and Dewettinck [21]

as well as interfacial crystallization, the presence of fine crystallites at the interface is further confirmed from the cryo-SEM image of freeze fracture sample where the water is removed through sublimation.

Emulsions were compared in terms of rheological properties, and as expected, the increase in the water phase led to an increase in the gel strength of emulsion (Fig. 5.2c). The moduli values (at lower % strain) showed an increase with the decrease in the fat phase (and the corresponding increase in the phase volume of dispersed water phase). The increase in the consistency of emulsions with increased water incorporation indicates that the increased interfaces contributes to the overall rheology of the emulsions. It is also important to note that the yielding behavior (yielding below 30 % strain) of emulsion with 60 %wt water was significantly different from other emulsions prepared at lower water contents, suggesting a comparatively brittle (plastic) structure of emulsion. The droplet size measured using diffusive NMR (Fig. 5.2d) suggested that the volume weighted mean droplet size (D33) for emulsion with 20 %wt water (~28 μm) was significantly lower than other three emulsions.

5.3 Complete and Partial Replacement of Oil Binder and Palm Oil in Chocolate Paste

Chocolate pastes are dispersions of cocao powder and sugar particles in oil continuous medium structured with considerable proportion of solid fat. Chocolate pastes have interesting rheological properties wherein they behave like an arrested 'soft' solid at rest to prevent sedimentation of dispersed particles as well as separation of liquid oil ('oiling out') and at the same time display a more liquid-like spreading capability (yielding) under applied force. This viscoelastic behavior of chocolate paste is achieved by incorporating significant amount (>20 %wt) of solid fats (hydrogenated oils or natural oils with high levels of saturated fatty acids such as palm oil) in the recipe. In addition, specialized ingredients such as oil binder (fully hardened vegetable fat) is also used to prevent 'oiling out' at storage temperatures. The possibility of complete replacement of oil binder and partial replacement of palm oil with SW oleogel was evaluated by preparing paste formulation as per the recipe given in Table 5.1. SW (at 1.5 %wt of total formulation) was added to chocolate paste in form of an oleogel which meant that in addition to complete replacement of oil binder, the palm oil was also partially replaced (~27 %) with liquid rapeseed oil resulting in more than 30 % SAFA reduction. As expected, due to the replacement of palm oil, the oleogel paste had a much softer texture compared to reference paste. However, even at low amount of solid fat and absence of oil binder, SW was effective in binding the oil samples as confirmed from the results of accelerated stability where the oleogel paste did not show any sign of 'oiling out' even after 4 weeks of storage at elevated temperature (30 °C).

Table 5.1 Recipe used for preparing reference and oleogel-based chocolate pastes

Ingredients	Reference paste (%)	Oleogel paste (%)
Sugar	48.85	48.85
Cocoa powder	7	7
Skimmed milk powder	8	8
Hazelnut paste	12	12
Palsgaard® PGPR 4125	0.15	0.15
Palsgaard® AMP 4448	0.5	0.5
Palsgaard® OilBinder 01	1.5	–
Shellac	–	1.5
Palm oil	22	16
Rapeseed oil	–	6
Total	100	100

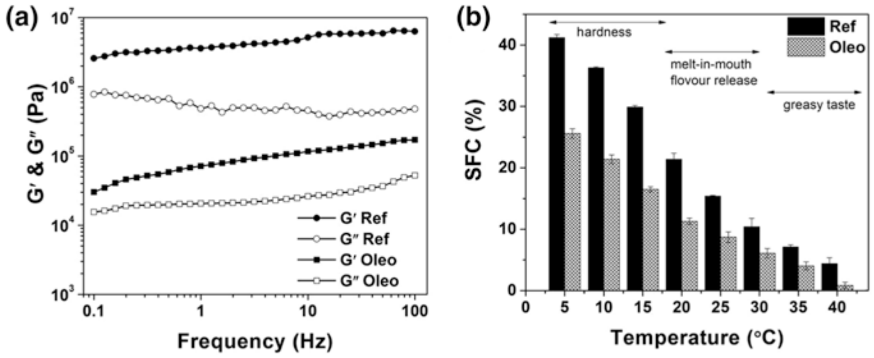

Fig. 5.3 **a** Oscillatory frequency sweeps for reference and oleogel pastes; **b** Solid fat content (% SFC) plotted as a function of temperature for reference and oleogel pastes. The SFC profile is roughly segregated into three temperature ranges along with the corresponding properties that are influenced

The viscoelastic properties of reference and oleogel paste were compared through oscillatory frequency sweeps (Fig. 5.3a). As seen from the graph, the comparatively softer structure of oleogel paste is clearly evident as both the G' and G'' were higher for reference paste as compared to oleogel paste. The G' was higher than G'' throughout the studied frequency range which indicates 'solid-like' behavior of both samples. However, in both cases, the G' was not independent of the applied frequency as confirmed from slightly positive slope of the curves. The frequency dependence of response suggests a weak gel structure [14].

Functionality and properties of fat-based products are usually defined by solid fat content (% SFC), and accordingly, most intermediate products (such as

Table 5.2 Rheological parameters obtained from flow curves

	↑σCA (Pa)	↑ηCA (Pa.s)	↓σCA (Pa)	↓ηCA (Pa.s)	Thixotropy (Pa)
Reference paste	9.7 ± 0.7	4.7 ± 0.3	7.4 ± 0.4	4.6 ± 0.4	5.8 ± 0.3
Oleogel paste	14.1 ± 0.8	3.3 ± 0.2	7.6 ± 0.3	3.4 ± 0.3	11.7 ± 0.5

Casson yield stress for *upward* and *downward* curves (↑σCA and ↓σCA, respectively), Casson viscosity for *upward* and *downward* curves (↑ηCA and ↓ηCA, respectively) and thixotropy. Reproduced from Patel et al. [8]

fat blends, hard stock, and bakery fats) and final products (such as margarine, spreads, and pastes) are characterized in terms of SFC profiles. SFC profile where % SFC is plotted as a function of temperature can be roughly segregated into 3 temperature ranges that influence the corresponding properties (5–20 °C = hardness; 20–30 °C = melt-in-mouth effect and flavor release; and >30 °C = greasy taste). SFC profile given in Fig. 5.3b clearly shows that higher amount of crystalline mass fraction is present in the reference as compared to the oleogel paste. The SFC was understandably lower for oleogel paste at all studied temperatures due to the decreased content of palm oil (saturated fatty acids ~49.8 %) which was replaced partially by liquid rapeseed oil (saturated fatty acids ~7.4 %) as well as the removal of oil binder which is a fully hardened fat. The lower SFC in the range of 5–20 °C clearly affects the firmness of the oleogel paste (as confirmed from oscillatory frequency sweeps), but most interestingly, the lower value of SFC >30 °C (more specifically between 35 and 40 °C) also confirms that oleogel paste is most likely to not have any greasy taste which is usually a drawback associated with oleogels prepared using high-melting waxes.

The rheological properties of these chocolate pastes were also compared using ICA46 (2000)—official method for chocolate rheology, to have more insights into their flow behavior. Flow parameters such as Casson yield stress (σCA), plastic viscosity (ηCA), and thixotropy (Table 5.2) were obtained by fitting the data from flow curves with Casson model. These parameters gives an indication of the flow of molten chocolate during processing and also the sensory attributes of finished products. Higher values of σCA and ηCA could pose certain issues during the processing of chocolate products [15, 16], while a significantly higher value for thixotropy in case of paste would mean that the sample would show poor structure recovery after spreading. In case of both oleogel as well as reference paste, the low plastic viscosity values were comparable. On the other hand, the yield stress (minimum stress required for a sample to yield or flow) was relatively higher for oleogel paste probably due to the higher interparticulate interactions among dispersed particles (sugar particles) because of lower solid fat content. Oleogel paste also exhibited a relatively higher thixotropy which can be attributed to the typical rheological properties of SW oleogels such as shear sensitivity (higher drop in viscosity with increase in shear owing to the structure breakdown) and partial structure recovery [13].

5.4 Oleogels as Shortening Alternatives

5.4.1 Functionality of Shortening

Shortenings are lipid-based, plastic, or quasi-plastic systems that derive their name from the 'shortening effect' they impart to end products. For baked products such as cakes, the 'shortening effect' refers to lubrication of particles and reduction of elasticity in cake batter. Specifically, the structured fat of shortening breaks the continuity of protein (gluten) and starch network in batter, consequently resulting in a tender, non-chewy texture of baked products [17]. The uniformly distributed shortening provides a thin lubricating film over tiny particles of cake mass, thus imparting long-lasting softness and freshness to cake products. In addition, the emulsifiers in shortenings further contribute to the stabilization of finer air bubbles in batter which results in end products with desired volume and uniform cell sizes. To summarize, the functions of shortening in batter and the corresponding properties imparted to baked products are as follows: a) lubrication (tender texture); b) aeration (volume and uniform cell structure); c) retain long-term softness (shelf life), and d) emulsify and hold water (prevent drying and retain moistness over storage) [17, 18]. To achieve these functions, a significant amount of shortening is used for baking applications, contributing heavily to the total calories and the fat content (which is sometimes refer to as 'hidden fats') of the end products. Since hydrogenated oils or natural oils high in saturated fats (such as palm oil) are used as hard stock for formulating shortenings, saturated fats constitute a high proportion of hidden fat contents in bakery products. The functionality of SW oleogel-based emulsion and polymer oleogel (described in Chap. 3, Sect. 3.3) was evaluated as shortening alternatives by comparing the intermediate (batter rheology) and end (cake texture and sensorial attributes) product properties as described in the following sections.

5.4.2 SW Oleogel-Based Emulsion as Alternative to Emulsified Shortening

Cake margarine, a type of emulsified shortening, is a special margarine designed for incorporation of a large amount of air and homogenous fat distribution in the batter, thus ensuring uniform expansion during baking and a resultant end product with homogenous crumb structure [19]. Crystallization in cake margarine is controlled in order to obtain small β' crystals of fats in the continuous oil phase as they increase the firmness and help incorporation of a large amount of air in the batter at a given solid fat content [20].

SW oleogel-based emulsion (SE) prepared by homogenizing 20 %wt water with oleogel (SW used at 10 %wt of total emulsion) was used as alternative to

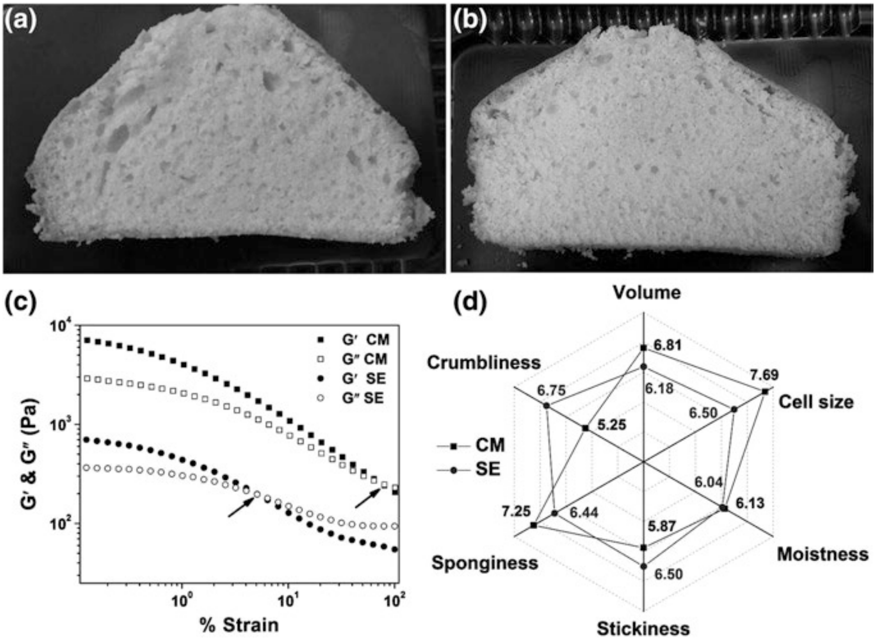

Fig. 5.4 (**a**, **b**) Photographs of cakes prepared using SE and CM as emulsified shortenings, respectively; **c** Comparative graph of G′ and G″ versus % strain for batter made using SE and CM as emulsified shortenings. The crossover points are marked with arrows. The measurements were carried out at 20 °C and a frequency of 1 Hz, and **d** Comparative sensorial parameters of SE and CM cakes. Only the differences in the cell size and crumbliness were found to be statistically significant ($p < 0.05$). Adapted from Patel et al. [8]

cake margarine (CM) in 4/4 sponge cake formulations. The batter and cake properties were compared using rheology, texture analysis, and sensorial aspects.

The absence of substantial amount of crystalline mass in SE led to a more runny consistency of batter made with SE as compared to the reference sample (prepared using CM) as also confirmed from a 10-fold difference in the G' (~7000 Pa for CM batter as compared to ~700 Pa for SE batter) along with a much lower yielding strain for SE (indicated by arrows in Fig. 5.4c). The decrease in the firmness of batter also had an influence on the air incorporation, resulting in a comparatively higher batter density (0.86 g/ml for SE batter as compared to 0.73 g/ml for CM batter). However, in spite of the difference in the consistency and density of the batters, the baked cakes (Fig. 5.4a, b) showed mostly comparable texture and sensorial attributes. Textural parameters such as firmness, springiness index, cohesiveness, and chewiness obtained from texture profile analysis (TPA) are listed in Table 5.3. Only springiness index and chewiness were found to be statistically different. Springiness index is defined as the ratio of height the sample springs back to after maximum deformation and is indicative of the elasticity of the sample. The higher values of springiness index of SE cake (0.72)

Table 5.3 Textural parameters obtained from TPA curves

Parameters	CM cake	SE cake
Firmness (N)	4.05 ± 0.31	3.48 ± 0.23
Cohesiveness	0.69 ± 0.02	0.64 ± 0.01
Adhesiveness (N.mm)	$-0.003 \pm 1 \times 10^{-3}$	$-0.004 \pm 1 \times 10^{-3}$
Springiness index[a]	0.43 ± 0.01	0.72 ± 0.01
Chewiness[a]	1.33 ± 0.09	2.23 ± 0.11

[a] Difference is statistically significant ($p < 0.05$). Reproduced from Patel et al. [8]

compared to the CM cake (0.43) can be related to the increased elasticity of the SE cake probably due to higher level of protein cross-linking in the batter. The elasticity of SE cake is also reflected from comparatively higher values of chewiness in SE cakes (Table 5.3).

The results from sensorial evaluation (Fig. 5.4d) indicated that SE cake was comparable to the CM cake for all studied parameters except for two related parameters of uniformity in cell size and crumbliness. The lower uniformity in cell size or voids for SE cake is due to the uneven distribution of air bubbles in the batter which are not efficiently stabilized due to the lack of solid fat crystals in the batter matrix. The non-uniformity of these air pockets also makes the cake less coherent and crumbly, leading to the formation of crumbs while handling of the cake. However, other properties of cakes such as sponginess and moistness that relates to the mouth feel were comparable, suggesting that there is potential for using emulsifier-free, SW oleogel-based emulsion as shortening alternative.

5.4.3 Polymer Oleogel as Alternative to Full-Fat Shortening

Apart from emulsified shortening described in previous section, full-fat, water-free shortenings are also used for baking purposes. In this work, polymer oleogel (containing 97.72 %wt sunflower oil) prepared using indirect emulsion-templated approach (with methylcellulose and xanthan gum as structuring polymers) was used as alternative to commercial shortening (CS). The batter properties (density, rheology, and microstructure studies) and cake attributes (texture and sensory analysis) were studied for oleogel-based cakes using commercial shortening and oil as positive and negative references, respectively.

As seen from rheology data (Fig. 5.5a–c), the oil batter showed a dominant 'liquidlike' behavior as confirmed from the values of damping factor ($\tan\delta = G''/G'$) above unity, yield stress (σ_y) of less than 2 Pa, and a low recoverable strain ($\gamma_e = 35$ %). On the other hand, the higher values of complex modulus (G^*), σ_y (4.81 Pa), and γ_e (56.3 %) suggest that CS batter was well structured. The rheology of oleogel batter was quite interesting, the structure was more close to CS batter (σ_y (4.64 Pa) and γ_e (43.3 %) but it was runny in nature like oil batter. This could provide dual advantages in terms of ease of pumping the batter in the processing

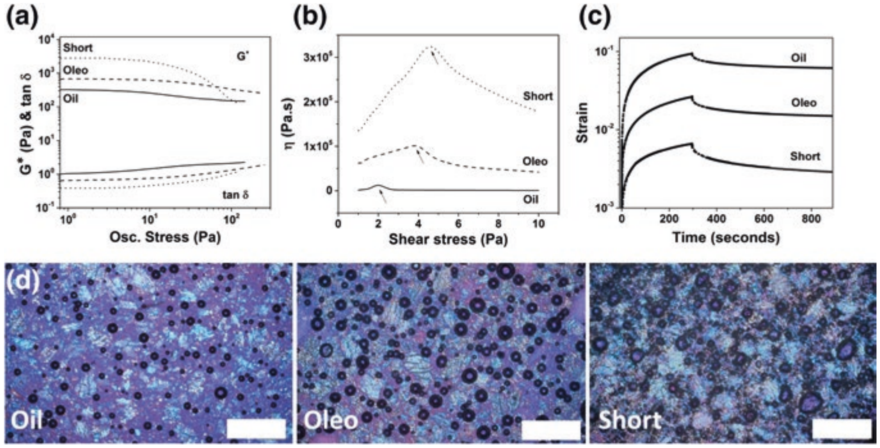

Fig. 5.5 (**a–c**) Batter properties compared using stress sweeps, stress ramp, and creep recovery tests, respectively; *yield points* are indicated by *arrows* and **d** Polarized light microscopy images of batters prepared using oil, oleogel, and CS as shortenings. (Scale bars: 200 μm). Adapted from Patel et al. [7]

lines while still resulting in cake with desired texture. The most prominent difference in the batter microstructure that can be noticed from polarized light microscopy images (Fig. 5.5d) is the presence of air bubbles: The oil batter showed least air incorporation compared to oleogel and CS batters which is also reflected in the values of batter densities (1.08 g/ml for oil batter compared to 0.92 and 0.84 for oleogel and shortening, respectively). The stabilization of air bubbles in shortening samples batter can be attributed partially to the presence of emulsifiers, whereas polymer oleogel had no added emulsifiers but still resulted in reasonable air incorporation probably because of the presence of surface active methylcellulose which could stabilize air bubbles in the batter matrix. The microscopy images of batter gets less dense and the batter solids (starch granules and sugar crystals) get more spaced out as we move from left to right in Fig. 5.5d. The dense appearance of images is an indication of structured oil systems forming a network in the matrix that stabilizes the particulate interactions as well as the incorporated air bubbles.

The baked cake products (shown in Fig. 5.6a) were subjected to TPA to compare their properties. Generally, it is possible to obtain good cakes with using oil as shortening, but the main problem with such cakes is the loss of ‘freshness’ or ‘quality’ over storage (i.e., increase in hardness, chewiness and moistness in time). Hence, in the current study, cake samples were evaluated using TPA on the day of preparation (day 0) as well as after 2 days of storage at room temperature (day 3). On comparing the results (Fig. 5.6b), it is clear that oil cakes show increase in both hardness and chewiness over storage compared to CS cakes, while the decrease in the cohesiveness is much less than CS cakes. Consequently, the oil cakes become non-spongy and give a dry mouth feel, whereas CS cakes become more crumbly due to the loss of cohesiveness in the structure. Oleogel cakes, on

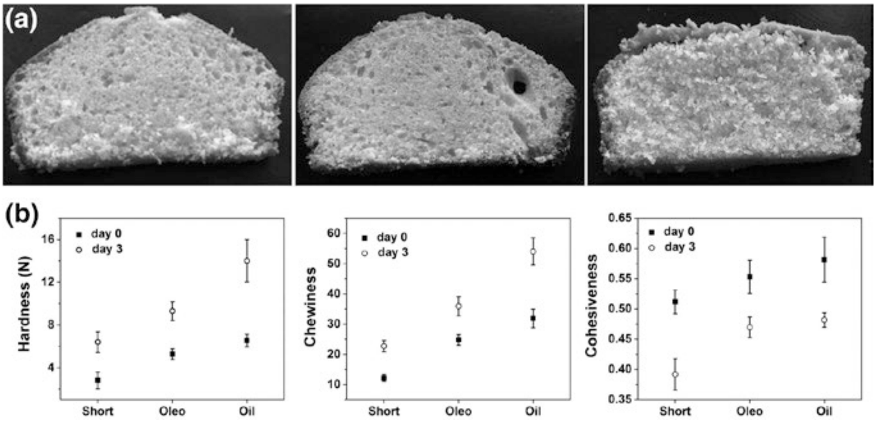

Fig. 5.6 **a** From *left* to *right*: Photographs of cakes prepared using oil, oleogel, and CS as shortenings and **b** Comparative textural parameters of cakes measured on the day of baking (day 0) and after 2 days of storage (day 3). Adapted from Patel et al. [7]

the other hand, displayed properties of both oil and CS cakes wherein they showed a low drop in cohesiveness (and a resultant decrease in crumbliness) as well as low increase in the hardness and chewiness values (retaining soft and pliant texture).

5.5 Conclusions

The potential of oleogels in diverse applications ranging from production of margarine and emulsifier-free spreads to stabilization of complex colloids (ice creams) and solid fat substitution in a range of products such as chocolate pastes, cakes, and comminuted meet products have already been demonstrated. Although oleogelation approach have definitely shown a huge potential as a possible solution for reduction of saturated fats, there are however certain limitations that need to be addressed in order to see the eventual transformation of laboratory research into commercial products. Most importantly, it should be known that a complete replacement of solid fats with gelled oil systems will most certainly lead to some loss of functionality. Thus, a further reworking of the formulation will be required to develop end products with required qualities.

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Chapter 6
General Considerations and Future Trends

Abstract Although, oleogelation as a strategy is still in its infancy, already a number of structurants have been investigated for oil gelling functionalities and some preliminary results on their applications in food formulations have also been reported. In this chapter, some of the most promising structuring systems have been discussed in terms of practical and general considerations associated with the processing protocols used for gel formation, properties of gelling agents, and the resulted effect on structuring, food-grade status, and regulatory issues. In addition, the properties of the structured systems with respect to shear sensitivity (and thixotropic recovery), thermo reversibility, appearance (optical clarity), and water tolerability (including emulsification) are also elaborated.

Keywords Hybrid systems · Oleogelators · Waxes · Food polymers · Mono and diacylglycerols · Ethyl cellulose · Phytosterols · Sterol esters

6.1 General Considerations

If the current trend is anything to go by, the interest in the area of oleogelation will continue to rise and more concrete applications of oleogels in real food systems will continue to be explored. Although oleogelation as a strategy is still in its infancy, already a number of structurants have been investigated for oil gelling functionalities and some preliminary results on their applications in food formulations have also been reported. The main bottleneck of this approach is identifying and selecting the right kind of structuring agent(s). In addition to the right structural features and molecular assembly properties (crystallization or supramolecular ordering), the identified structuring agent also needs to satisfy most (or preferably all) of the conditions listed below:

- should be a food ingredient and be approved for use as 'direct additive' or 'formulation aid'
- should be effective at low concentrations

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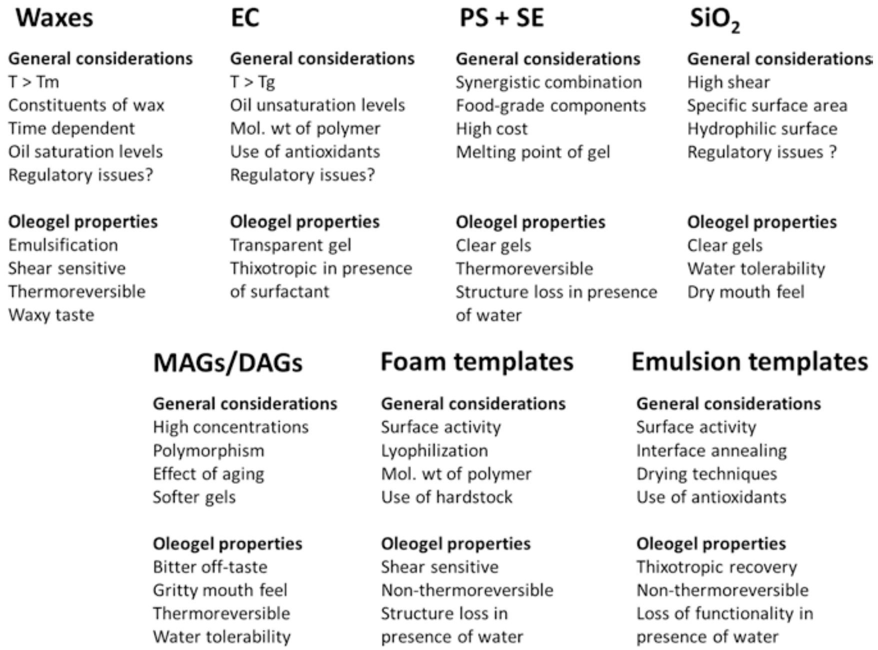

Waxes

General considerations
T > Tm
Constituents of wax
Time dependent
Oil saturation levels
Regulatory issues?

Oleogel properties
Emulsification
Shear sensitive
Thermoreversible
Waxy taste

EC

General considerations
T > Tg
Oil unsaturation levels
Mol. wt of polymer
Use of antioxidants
Regulatory issues?

Oleogel properties
Transparent gel
Thixotropic in presence of surfactant

PS + SE

General considerations
Synergistic combination
Food-grade components
High cost
Melting point of gel

Oleogel properties
Clear gels
Thermoreversible
Structure loss in presence of water

SiO_2

General considerations
High shear
Specific surface area
Hydrophilic surface
Regulatory issues ?

Oleogel properties
Clear gels
Water tolerability
Dry mouth feel

MAGs/DAGs

General considerations
High concentrations
Polymorphism
Effect of aging
Softer gels

Oleogel properties
Bitter off-taste
Gritty mouth feel
Thermoreversible
Water tolerability

Foam templates

General considerations
Surface activity
Lyophilization
Mol. wt of polymer
Use of hardstock

Oleogel properties
Shear sensitive
Non-thermoreversible
Structure loss in presence of water

Emulsion templates

General considerations
Surface activity
Interface annealing
Drying techniques
Use of antioxidants

Oleogel properties
Thixotropic recovery
Non-thermoreversible
Loss of functionality in presence of water

Fig. 6.1 Current understanding of oleogelation presented in the form of a comparative list of general considerations and properties of oleogels for different structuring systems

- should tolerate the processing conditions and be compatible with the formulation matrix
- should be low cost and easily available
- should provide the right functionality when used in intermediate products such as cake shortening or baking margarine and be capable of mimicking the melt-in-mouth type oral sensation (provided by fat crystals) when used in final products such as spreads and chocolate products.

Apart from the compliance of structuring agents to the above-mentioned conditions, the process used for structuring of oil should also be industrially feasible and not too energy intensive or harsh for the oils used (to prevent deterioration of oil quality).

In order to have a thorough understanding of these factors, some of the most promising structured oil systems are discussed in this section in terms of practical considerations and properties of the structured systems. A concise snapshot of this discussion is provided in Fig. 6.1 where structured systems based on waxes, ethylcellulose (EC), phytosterols + sterol esters (PS + SE), fumed silica (SiO_2), and mono- and diacylglycerols (MAGs and DAGs) are included along with the systems fabricated using indirect approaches such as foam and emulsion templates. Each of these systems is discussed individually below.

Waxes: Oil structuring using natural waxes has a lot of advantages including ease of process, efficient structuring at low concentrations, possibility of mimicking melting behavior of fats, and tolerability to water incorporation. Wax-based oleogels are prepared by simple process of heating waxes in liquid oil at temperatures above their melting points followed by cooling to room temperature under mild shear or quiescent conditions. The oil gelling properties of waxes are influenced by a number of factors including (a) constituents of waxes: Due to the presence of different components and impurities, waxes show variation in gelling behavior depending on the source, purification process, and time of collection [1, 2]; (b) oil quality: Usually, the higher the saturation levels of oils, the better the gelation. However, the gelation behavior of waxes cannot be always generalized based on saturation levels of oils, and some wax–oil combination shows very specific gelling properties [3]; and (c) time dependent: Since waxes are generally used at much lower concentrations, the crystallization kinetics plays a major role in defining the gel properties of formed oleogels.

The main advantage of wax oleogels is that they can be used as oil phase for fabricating water-in-oil-type structured emulsions with or without the use of added emulsifiers [2, 4, 5]. Moreover, the gels are thermo-reversible and accordingly are quite suited for food processing that involves temperature modulations. However, wax oleogels are known to undergo softening under shear followed by a poor structure recovery on removal of shear [5]. Additionally, a high concentration of wax (which is required in some cases to obtain the desired firmness and consistency) may give undesirable waxy mouthfeel, especially for waxes that have higher proportion of high-melting components. In addition, when considering the food applications, most waxes are approved only as indirect additives (coating or glazing agents) [6]. Thus, there may be regulatory restrictions for using waxes as direct formulation aids.

Ethyl cellulose (EC): EC is the only known food polymer which can be used for preparing oleogels through direct dispersion process. EC oleogels are self-standing gels with versatile properties, and they have been extensively researched in the last few years including their use in model food systems [7–9]. Among the factors studied for understanding gelation properties of EC, the molecular weight of EC (viscosity grade of polymer) was found to have a major influence on the mechanical strength of EC oleogels. Understandably, the gel strength increases with the increasing molecular weight of EC used in oleogel preparation [10]. It is also seen that the oil type plays a role in influencing the gel strength, with high unsaturation levels (especially with multiple double bonds) resulting in stronger gels as they provide better support for polymer chain–chain interactions [11]. However, the major limitation of EC oleogels is the energy-intensive process required for oleogel formation. Although prepared by direct dispersion process, the polymer dispersion has to be carried out at temperatures above the glass transition temperature (T_g) of EC which is in excess of 130–140 °C. To ensure the uniform dispersion of polymer, the process generally involves a certain holding time at high temperature which has known to cause deterioration of oil quality (oxidation) as well as the breakdown of polymer and surfactant [12]. Optimization of manufacturing conditions and use of antioxidants have been proposed as a possible solution to minimize the temperature effects and improve reproducibility of the mechanical strength of the formed gels [12]. EC oleogels are also sensitive to shear and are known to undergo irreversible loss in structure under shear. The thixotropic properties have been improved by incorporating a large amount of glycerol monooleate, albeit for non-food applications [13].

With regards to regulatory issues, EC has a GRAS status (generally recognized as safe) and is approved as food additive for indirect use [14]. For oleogel preparation, usually a concentration in excess of 6 %wt is used to obtain the desired firmness and texture. Such applications will not fall under the indirect usage category; thus, regulatory restrictions may apply.

Combination of phytosterols and sterol esters (PS + SE): Among the systems that are structured based on self-assembled building units, oleogels formed by mixtures of phytosterols and sterol esters (specifically β-sitosterol and γ-oryzanol) have received considerable interest, mainly because of the true food-grade nature of the components used. Synergistic interactions of β-sitosterol with γ-oryzanol are exploited to generate supramolecular assemblies in the form of tubules with dimensions in nanoscale range. Interestingly, these structures formed by mixtures are quite different from three-dimensional crystals formed by individual components [15]. The gels are formed by dispersing components in liquid oil at high temperature (to ensure complete dissolution of components) followed by cooling to ambient temperature. Depending on the total sterol concentration, the gelling time may be delayed, especially when used at lower concentrations (below 10 %wt) [16]. The gelling process is reversible, and the gels can be melted and regelled by applying new heating and cooling cycles. Due to the fine size of building units (i.e., tubules), the resultant gels are transparent to slightly hazy transparent in appearance. The gel properties are mainly affected by the proportion of components used in gel preparation, and a 1:1 molar ratio of sitosterol and oryzanol results in gels with maximum firmness. These oleogels are among the most systemically investigated structured systems, and many attractive properties of these systems have been demonstrated. However, the main limitation of these oleogels is their sensitivity to water. Since tubules are formed due to intermolecular hydrogen bonding, the introduction of water interferes with tubule formation and results in the formation of β-sitosterol monohydrate crystals. Another limitation of these systems is the requirement of high concentration of components to achieve desired firmness. At such high concentrations, the melting point of gels is much higher than body temperature [17]. In addition, these components are rather expensive, which implies that their usage is limited to relatively niche applications [15].

Silicon dioxide (SiO_2): Recently published research on fumed silica-based oleogels [18] demonstrates that inorganic particles can also be used as structuring units in addition to the other well-known building blocks such as crystalline particles, polymeric strands, and self-assembled structures such as tubules and fibrils. The process of gel formation involves direct dispersion of fumed silica in liquid oil at ambient temperature under shear. The gelling mechanism involves first the deagglomeration of fumed silica into aggregates of primary particles followed by reassociation of these uniformly dispersed aggregates, resulting in a continuous network formation. Firm, optically clear gels are obtained at concentration of 10 %wt and above. The main requirement of gel formation (apart from critical gelling concentration) is the use of high shear (≈11,000 rpm using high-energy-dispersing unit such as Ultra-Turrax®) in order to achieve proper deagglomeration and uniform dispersion of silica particles. The fractal-like aggregation of silica particles into an open network structure is attributed to high specific surface area of fumed silica (which is responsible for high oil absorption) as well as surface chemistry (presence of hydrophilic hydroxyl groups). Due to the hydrophilic nature of particles, the incorporation of water results in weakening of the oleogel structure. However, when water is introduced as 'weak gel' (structured using food hydrocolloids such as locust bean gum and carrageenan), interesting bicontinuous microstructure is obtained due to the arrested demixing process. The resultant bigels stabilized by interpenetrating networks of structured water and oil phases have better rheological properties compared to monocomponent gels—oleogel and water gel. The low-temperature processing, optical clarity of gels, and water tolerability provide enough advantages to these systems. Silicon dioxide is an approved food ingredient for specific roles such as carrier, lubricant, and anti-foaming and anti-caking agent in a wide range of food products with a maximum level of 10–15 g/kg [19]. However, the use of SiO_2 as a direct formulation aid may require further regulatory approval. Moreover, when placed on tongue, the hydrophilic silica particles in oleogels tend to rapidly absorb saliva, giving rise to a dry mouthfeel. The dry mouthfeel is not so much of an issue in bigels which already contains water phase.

Mono- and diacylglycerols (MAGs and DAGs): Due to their structural features, partial glycerides (MAGs and DAGs) are comparatively much more polar than triacylglycerols (TAGs), and thus, their crystallization behavior is quite different from TAGs although they all belong to the acylglycerol family (i.e., fatty acid esters of glycerol). Both MAGs and DAGs are known to form crystalline network in liquid oils, which results in gel formation (although the gels are bit softer than TAG gels at same concentrations) [20, 21]. Since these partial glycerides are already being used in food industry as direct additives without any specified maximum limits (*quantum satis)*, MAGs and DAGs can be considered to have a better acceptance compared to all the other studied structurants. In addition, owing to the interesting phase behavior displayed by MAGs in oil–water mixtures, a range of oil–water gelled systems can be easily produced [22, 23]. In fact, the 'fat-like' properties of these gels have already been used for commercial applications (marketed under the brand CoaSun™) [24]. As far as water-free oil gels are concerned, a relatively high concentration of MAGs (≫10 %wt) is required to achieve desired texture and rheology. At such high concentrations, the palatability of structured systems could be unacceptable due to the strong bitter-off taste. Moreover, MAGs are also known to undergo polymorphic transformation to more stable β-crystals in time leading to physical instability (phase separation) [25] or gritty texture on aging.

Foam and emulsion templates: Indirect approaches such as foam and emulsion-templated processes are used to exploit structuring properties of hydrophilic polymers (with surface active properties) which cannot be dispersed directly in liquid oils. In principle, the main aim is to achieve prehydration of polymers in aqueous phase followed by selective solvent drying in order to obtain structural framework made up of dried extended polymer sheets and strands [26, 27]. The most attractive feature of these indirect approaches is the possibility of using a hydrophilic food polymer including biopolymers such as proteins and modified polysaccharides for oil structuring. Since a wide range of polymers are approved for food applications, these indirect approaches hold significant promise in extending oleogelation strategy to actual commercial applications. However, the main drawback associated with these approaches is the water removal step which requires either energy-intensive process such as lyophilization or exposure of system to high temperatures for long time which consequently results in deterioration of oil quality. At least for emulsion templates, alternative dry technique such as spray drying can be used [28] along with the use of antioxidants to minimize oxidation-related issues. Similar to EC oleogels, the mechanical strength of structured oil systems created using these indirect approaches is strongly influenced by the molecular weight of the polymer used [29, 30].

The gels prepared from these approaches are thermostable, i.e., they cannot be reversibly melted and restructured using temperature as a trigger. In addition, due to the hydrophilic nature of polymers, the structured systems are very sensitive to water. For instance, incorporation of water (as little as 5 %wt) in gels prepared from foam templates shows immediate polymer aggregation followed by phase separation, while incorporation of water and subsequent shearing of emulsion-templated gels result in the formation of water-continuous emulsions [26, 31]. The emulsion-templated gels are not shear sensitive and show reasonable thixotropic structure recovery on removal of shear. On the other hand, the foam-templated gels show very limited structure recovery. However, based on recent trails, we have found that the problem of structure recovery can be easily solved by incorporating small amount of crystalline phase in the gels as discussed in Chap. 3, Sect. 3.2.2.

6.2 Conclusions and Future Trends

In the previous section, some of the most promising structuring systems have been discussed in terms of practical and general considerations associated with the processing protocols used for gel formation, properties of gelling agents and the resulted effect on structuring, food-grade status, and regulatory issues. In addition, the properties of the structured systems with respect to shear sensitivity (and thixotropic recovery), thermo-reversibility, appearance (optical clarity), and water tolerability (including emulsification) were also elaborated. After taking into account the advantages and disadvantages of several structured systems, some generalized conclusions can be made as follows:

(a) Some of the most efficient structurants capable of showing gelling at low concentrations and resulting in gels with desired fat-mimicking properties may not have the required food approval to be used as direct additives. Hence, additional regulatory clearance will be needed in order to use these structurants.

(b) Sophisticated and energy-intensive processes (lyophilization, high-temperature dispersion, and spray drying) are required in order to use non-lipid, non-crystalline components (such as food polymers) as structurants. It is quite straightforward to imagine that the industrial acceptance of these structured systems will only happen if the possible benefits of the structured systems outweigh the additional cost investment.

(c) A complete replacement of solid fats with structured oil systems will not be possible without some loss in the properties (either reduction in mechanical strength or increased water sensitivity or a falloff in the mouthfeel). Thus, some amount of reformulation and reworking will be necessary to reach the desired attributes. For instance, instead of aiming for 100 % solid fat replacement, hybrid systems (where oleogelation is combined with a small amount of solid fats) could be created to achieve desired product attributes and substantially lower solid fat contents.

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