



# Water-in-Oleogel Emulsions—From Structure Design to Functionality

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The development of water-in-oleogel (W/Og) emulsions is highlighted, with focus placed on the key properties dictating the structuring ability of both the continuous oleogelled and dispersed phases present. The gelling ability of oleogelators is distinguished by the formation of crystalline structures, polymeric strands, or tubules. Once a dispersed aqueous phase is introduced, droplet stabilization may occur via oleogelator adsorption onto the surface of the dispersed droplets, the formation of a continuous gel network, or a combination of both. Surface-active species (added or endogenous) are also required for effective W/Og aqueous phase dispersion and stabilization. Processing conditions, namely temperature-time-shear regimes, are also discussed given their important role on dispersed droplet and oleogel network formation. The effects of many factors on W/Og emulsion formation, rheology, and stability remain virtually unknown, particularly the role of dispersed droplet size, gelation, and clustering as well as the applicability of the active filler concept to foods. This review explores some of these factors and briefly mentions possible applications of W/Og emulsions.

**Keywords:** oleogel, water-in-oleogel emulsion, emulsifier, active filler, inactive filler

## INTRODUCTION

Much has been written about emulsion gels and the role of their dispersed and continuous phases on texture and rheology. Research efforts have centered on oil-in-water (O/W) emulsion gels, with far less attention paid to structured water-in-oil (W/O) emulsions (Rafanan and Rousseau, 2019; Wijarnprecha et al., 2019a,b). Many W/O emulsions are stabilized by the presence of a continuous fat crystal network that confers desirable texture, palatability, and functionality. Driven by human health concerns, ingredient sourcing, and consumer acceptability, alternate ways of solidifying the oil phase via oleogelation have come to the forefront (Hughes et al., 2009; Davidovich-Pinhas et al., 2016).

From a food structure design perspective, most processed foods are complex mixtures of building blocks that result in composite materials with distinctly different properties compared to their starting components. This mini-review focuses on the recent progress made in oleogelator-stabilized W/O emulsion gels [water-in-oleogel emulsions (W/Og)], with a focus on the properties of the oleogelators used to create a network in W/Og systems as well as those of the dispersed phase and oil-water interface. An understanding of the contributions of the different phases in W/Og systems offers a pathway to the effective design of these structured emulsions.

## DESIGNING W/OG SYSTEMS

### Oleogelator Characteristics

The replacement of solid fat in the continuous phase of a W/O emulsion by an oleogel is a novel structuring approach that contributes to lower caloric value and saturated fat content (Scholten, 2017). It is well-known that oleogelators can be used to entrap liquid oil into a self-assembled network of weakly-interacting species (Hu et al., 2015). Upon introduction of a dispersed water phase, however, the oleogelator network must also prevent water droplet coalescence and phase separation, which may be achieved in one of two ways. Via network stabilization, the oleogel matrix encases the dispersed phase and acts as a physical barrier between neighboring droplets. When the oleogelators adsorb to the droplet surface, the resulting interfacial film may limit coalescence, as seen in fat crystal-stabilized W/O emulsions (Ghosh et al., 2011). In this regard, certain emulsifiers may not only affect the kinetics of oleogelator solidification in the bulk, but also interactions between oleogelators and dispersed droplets. Their ability to do so will depend on parameters such as emulsifier concentration, molecular weight, solubility, and molecular compatibility with the oleogelator molecules.

### Crystal-Based W/Og Systems

Crystal-based W/Og stabilizers often consist of waxes and, to a lesser extent, emulsifiers, or fatty acids. Sources of wax include rice bran, beeswax, candelilla, shellac, or sunflower. Typically, these consist of long chain fatty acids, or alcohols and wax esters, along with minor compounds such as ketones or aldehydes. Upon cooling, different crystal morphologies may arise, whose shape and size will depend on the inherent wax composition, solvent type, and processing parameters such as cooling and shear regime (Doan et al., 2018).

Certain waxes may also promote formation of kinetically-stable W/O emulsions (Binks and Rocher, 2009; Patel et al., 2013). As little as 2 wt% shellac wax in oil, for example, was shown to stabilize W/Og systems containing a 20 wt% dispersed aqueous phase. Stability arose from the formation of droplets <5  $\mu\text{m}$  in diameter and the presence of small wax crystals at the water droplet surface (Patel et al., 2013). In another study, 10 wt% rice bran wax in oil was used to form and stabilize W/Og systems. Here, stability was conferred by long, needle-like wax crystals present on both the surface of dispersed droplets and in the continuous phase (Wijarnprecha et al., 2019a).

Using waxes as the sole emulsifying agent generally remains challenging as these often lack the necessary surface-active compounds. Efforts to surmount this problem have focused on hybrid systems consisting of wax and an appropriate emulsifier to generate and stabilize kinetically-stable W/Og systems. Toro-Vazquez et al. (2013) found that the use of monoacylglycerols in W/Og systems stabilized by 2 wt% candelilla wax reduced droplet size, but also decreased hardness even though the final solids content with added emulsifier was higher. They ascribed this to weakened crystal-crystal interactions (Toro-Vazquez et al., 2013). In a study on crude oil, Ma et al. (2017) found evidence of synergy between paraffin wax and

sorbitan monooleate, which facilitated the adsorption of wax crystals onto the surface of aqueous droplets, resulting in an increased interfacial elastic modulus. Similarly, Haj-shafiei et al. (2013) found that the combination of paraffin wax and glycerol monooleate yielded kinetically-stable W/Og systems with controllable droplet size, as opposed to the use of wax alone.

Besides waxes, other species may be used to stabilize W/Og systems. Using a combination of soy lecithin and stearic acid at up to 30 wt% of the oil phase, Gaudino et al. stabilized W/Og systems containing up to 20 wt% dispersed water. The authors described a mixed system wherein the lecithin formed worm-like micelles that stabilized the stearic acid-covered water droplets (Gaudino et al., 2019). In another study, Hughes et al. found that use of 2 wt% 12-hydroxystearic acid could effectively stabilize W/Og emulsions containing a 10 or 20 wt% dispersed aqueous phase. The resulting system consisted of large, polydisperse water droplets solely stabilized by the surrounding oleogelled network. Addition of an emulsifier decreased droplet size, but also hampered gel formation (Hughes et al., 2009). Such studies demonstrate the need for added emulsifiers or the presence of endogenous surface-active species for effective W/Og system formation and stabilization (Beri et al., 2013).

### Fibril-Based W/Og Systems

A number of fibrillar oleogelator networks have been used to stabilize W/Og systems. These either consist of polymers or small molecules that form thin fibers with a high aspect ratio under optimized processing conditions. Using the well-known combination of  $\beta$ -sitosterol and  $\gamma$ -oryzanol for oleogelation, Bot et al. showed that 30 wt% water could be dispersed within a network of fibers that adsorbed onto the water droplet surface and also structured the continuous phase (Bot et al., 2011). Ethylcellulose (EC) is another oleogelator that forms long crosslinked, fiber-like structures, and whose rheological properties also depend on solvent type and molecular weight (Davidovich-Pinhas et al., 2016). This polymer was shown to form oil-continuous emulsion gels using propylene glycol as the dispersed phase. Although not visualized directly, it was hypothesized that the EC adsorbed onto the surface of the dispersed droplets, as well as providing network stabilization (Ceballos et al., 2014). In a study using 2-octyldodecanol as the oil phase and EC, temperature was found to play a key role on emulsion gel formation. Emulsification at 15°C resulted in a solid-like, oil-continuous structure whereas at 30°C, phase inversion was observed. The authors concluded that the EC formed colloidal particles that adsorbed to the oil-water interface, rather than fibers, and stated that temperature-dependent EC solubility in oil led to the formation of either a water or oil-continuous emulsion (Melzer et al., 2003). Finally, Munk et al. found that EC could be used to stabilize O/W emulsions when emulsification took place at temperatures below the melting point of the oleogel (Munk et al., 2019).

### Dispersed Phase Contributions

Aqueous droplet properties to consider in regards to W/Og system functionality include the dispersed phase droplet size

and distribution, volume fraction, extent of interaction with neighboring species, state of aggregation, and rigidity (either of individual droplets or clusters), as studied in O/W emulsion gels (van Vliet, 1988; Scholten, 2017). In such systems, it was found that dispersed droplet size directly contributed to large deformation behavior (Sala et al., 2009). Fuhrmann et al. found that clustering of dispersed oil droplets increased viscosity up to three orders of magnitude due to the increase in effective volume fraction (Fuhrmann et al., 2019). Elsewhere, effective clustering of oil droplets could increase O/W emulsion gel rigidity in a controllable manner (Oliver et al., 2015; Van Aken et al., 2015). In W/Og systems, however, controlling such parameters remains virtually unexplored. Decades ago, Pal showed that a reduction in aqueous droplet size increased the viscosity of concentrated W/O emulsions (Pal, 1996), and he also showed that combining small and large droplet sizes greatly affected emulsion viscosity and small deformation (Pal, 1996). Droplet clustering is likely to be an important factor in W/O emulsion viscosity (Liu et al., 2016), which also warrants its scrutiny in W/Og systems.

### Droplet Interactions With the Oleogel Matrix

The structure and rheology of a W/Og system will depend on the type and extent of interactions between the surface of dispersed aqueous droplets and the surrounding oleogel. As active fillers, droplets interact with the oleogel matrix and enhance W/Og rigidity and resistance to deformation, which occurs more readily when the dispersed droplets are stiffer than the gel network. As inactive fillers, aqueous droplets show little or no interaction with the surrounding oleogel, and either have no effect on, or reduce, W/Og rigidity.

#### Active Fillers

Affinity between droplet-bound emulsifier molecules and the surrounding oleogel matrix can play a significant role in determining whether droplets behave as active or inactive fillers. Effective emulsifier adsorption and molecular alignment on the droplet surface increases the likelihood of the ordering of oleogelator species close to the droplet surface, possibly through heterogeneous nucleation and interfacial templating of surrounding oleogelators present in the continuous phase. In this scenario, the resulting aqueous droplets are active contributors to the texture and rheology of the surrounding volume-spanning oleogel network. For instance, Wijarnprecha et al. showed that droplet-bound monostearin crystals acted as heterogeneous nucleation sites for continuous phase rice bran wax crystals in W/Og systems, resulting in the dispersed aqueous phase acting as an active filler (Wijarnprecha et al., 2019a). Using monoacylglycerols for emulsification and a combination of candelilla wax and fully hydrogenated fats to stabilize W/O emulsions, da Silva et al. showed that adding up to 20 wt% water increased W/Og rigidity, with higher proportions of water having a limited effect on rigidity compared to the control (da Silva et al., 2019). Interestingly, in contrast to Wijarnprecha et al. they also found that addition up to 5 wt% water substantially increased rigidity,

which the authors attributed to a reduction in crystal size (Wijarnprecha et al., 2019a).

#### Inactive Fillers

In many cases, incorporating aqueous droplets within an oleogel will structurally weaken the resulting W/Og, even when there are interfacially-bound oleogelator species or emulsifiers present (Patel et al., 2013). Much of this may be ascribed to poor emulsifier interfacial ordering or lack of molecular compatibility with neighboring oleogelator species in the continuous oil phase. For instance, in a study on lipstick-like wax-stabilized W/O emulsions where the oligomeric emulsifier polyglycerol polyricinoleate (PGPR) was used as the emulsifier, the storage modulus of the matrix alone was higher than that of the composite emulsion (Le Révérend et al., 2011). In this case, the droplets acted as inactive fillers given their lack of interaction with the matrix and low viscosity. In EC-stabilized W/Og systems, increasing the dispersed phase volume fraction decreased the hardness of the emulsion gels obtained, which was attributed to interference of polymer gel structure by the dispersed droplets (Ceballos et al., 2014). Similarly, when PGPR was used to stabilize W/Og systems using rice bran wax as the oleogelator, dispersed droplets did not interact with the gel matrix resulting in a decrease in W/Og rigidity (Wijarnprecha et al., 2019b). In this case, it was shown that wax crystals were indeed the only structuring agent, as replacing water droplets with an equivalent amount of liquid oil did not alter overall gel network strength. Yet another example of inactive fillers used a phytosterol-stabilized emulsion gel, with glycerol as the dispersed phase (Matheson et al., 2018). Glycerol droplets acted as inactive fillers due to a lack of anchoring to the surrounding fibrillar gel network, which weakened the overall structure.

### Structuring the Internal Water Phase

The gelation of the dispersed aqueous phase present in W/Og systems is an alternate route to limit the “destructuring” effect of adding water droplets. By gelling the internal water phase, these droplets become stiffer, and limit any weakening effect. Iqbal et al. (2019) explored the gelation of the dispersed aqueous phase of W/O emulsions using different kinds of polysaccharides (high-methoxy pectin, kappa-carrageenan, and starch). Alexa et al. (2010) found that addition of  $\kappa$ -carrageenan to W/O spreads resulted in an altered microstructure with larger aqueous droplets, but did not affect overall rigidity. Recent work has shown that the stability of gel-in-gel W/O high internal phase emulsions (HIPEs) resulted from the combined presence of a highly-packed dispersed aqueous phase stabilized by carrageenan, glycerol monooleate at the oil-water interface, and a surrounding beeswax crystal network (Lee et al., 2019). Ono et al. developed HIPEs that comprised silicone oil and water prepared with low concentrations of a glucose-based gelator that gelled both the dispersed and continuous phases, which resulted in HIPEs with tunable rigidity (Ono et al., 2018). Other work looked at the effect of xanthan gum in the aqueous phase of beeswax-stabilized W/Og systems, but no clear effect on overall properties was established (Öğütçü et al., 2015).

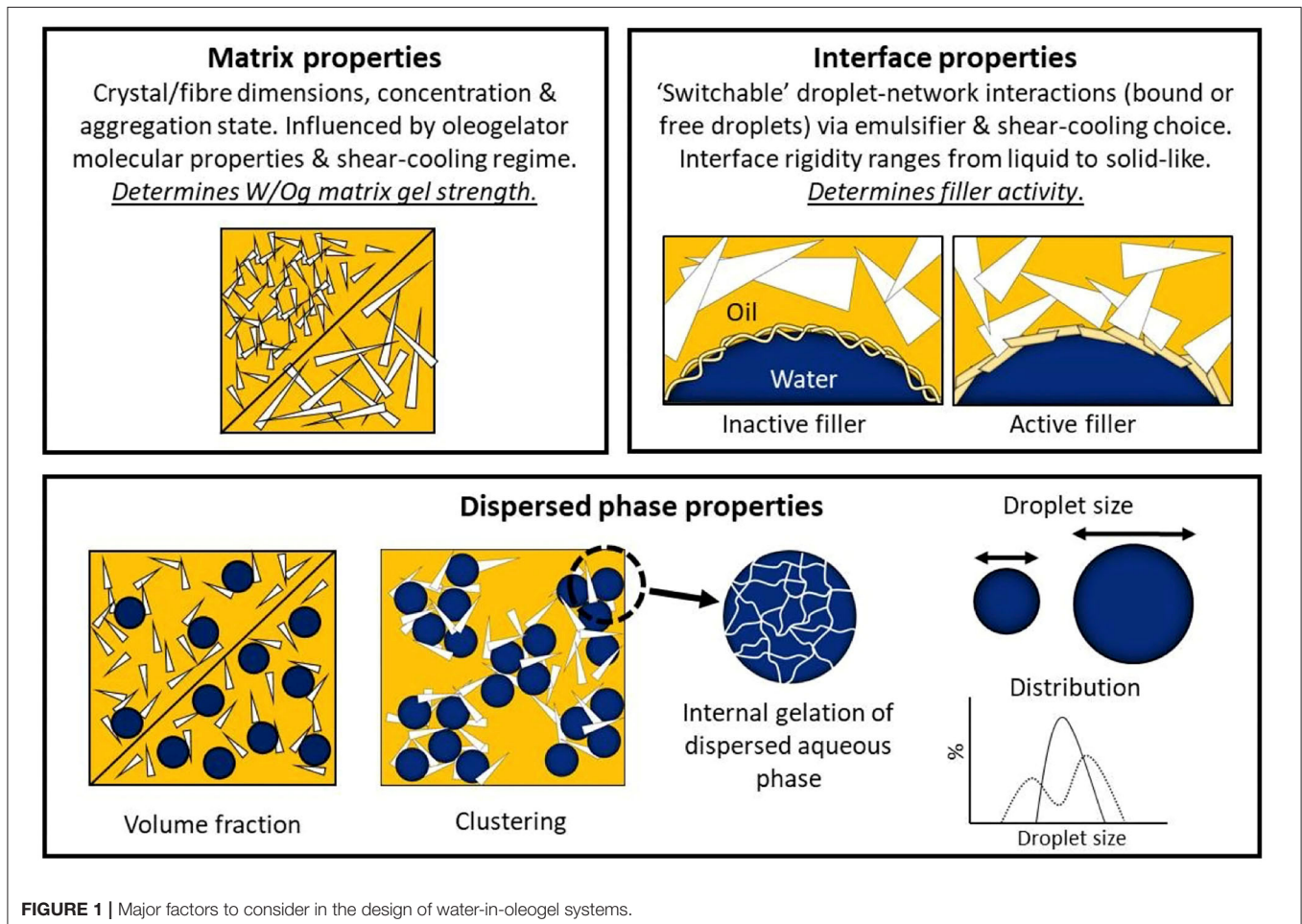
## Processing Parameters to Tune W/Og Properties

Emulsion processing parameters such as shear and cooling rate will directly affect the physical properties of W/Og systems. Using a combination of glycerol monooleate and paraffin wax to stabilize W/O emulsions, Ghosh et al. (2015) found that altering cooling rate [slow (1°C/min) vs. fast (5°C/min)], end temperature (25 or 4°C) and the presence/absence of shear during cooling had a marked effect on final W/Og properties. They noted that the presence of wax crystals at the oil-water interface was promoted when cooling at 5°C/min in combination with agitation (Ghosh et al., 2015). When comparing cooling rates of 1 or 10 °C/min, Patel et al. (2013) found that a larger number of smaller shellac wax crystals were formed using a higher cooling rate, which led to stronger crystal–crystal interactions and network formation. Using different wax sources, Binks and Rocher showed that emulsion stability was affected by emulsification and storage temperatures (Binks and Rocher, 2009). Here, wax crystallized at the oil-water interface gave rise to enhanced emulsion resistance against breakdown compared to pre-adsorbed crystals. This was also shown by Rousseau and Hodge, where post-emulsification crystallization of paraffin wax yielded W/O emulsions that were noticeably more stable against

physical breakdown than with pre-crystallized wax—a finding attributed to the smaller wax crystal size with post-crystallization (Rousseau and Hodge, 2005). When summarized, these findings show that processing conditions related to temperature-time-shear regimes can be used to not only tune droplet size and stability, but also the location of the oleogelator—either in the continuous phase, at the droplet surface, or both. Results to-date suggest that processing regimes that promote smaller average droplet sizes and narrower size distributions along with the presence of interfacially-bound species will promote W/Og emulsion stability against coalescence and phase separation.

## SUMMARY AND FUTURE PROSPECTS

**Figure 1** summarizes many of the key parameters used to tune the rheology and structure of W/Og systems. Gel matrix functional attributes can be controlled by oleogelator type, concentration, crystal/fiber size, and aggregation state. Properties of the dispersed aqueous phase, including volume fraction, clustering, droplet size, and size distribution and possible gelation may alter the final properties of the W/Og system. Structuring the interface into a solid-like film can be responsible for making liquid, spherical inclusions behave as solid particles (Van Aken



**FIGURE 1** | Major factors to consider in the design of water-in-oleogel systems.

et al., 2015). Finally, processing conditions, namely temperature-time-shear regimes, can be used to tune the properties of both the oleogel and aqueous phases.

The surface of aqueous droplets can be selectively tailored toward attractive interactions between the matrix and the surface of the droplet. This is the central tenet of the filler concept, which has been extensively explored in gelled O/W emulsions, but which remains virtually unexplored in W/Og systems. Similar to water-continuous emulsions, it is presumed that dispersed water droplets in an oleogelled matrix will only act as active fillers when the modulus of the dispersed phase is higher than that of the matrix. In practice, this might be difficult, as typically, the elastic modulus of fat-continuous gels is higher than those in water-continuous systems. In most wax-based W/Og systems, for example, there exists a relatively strong crystal network and addition of water droplets would only weaken the composite. Moreover, since the modulus of the dispersed phase is affected by droplet radius, W/Og systems are at a disadvantage since emulsified water droplets are more often larger than oil droplets.

A further complicating factor is that addition of water droplets or emulsifiers to oleogels can alter several W/Og properties at once, e.g., wax crystal size and 3D spatial arrangement, which makes direct identification of the contributions of the dispersed phase to W/Og behavior more difficult. Similarly, processing parameters such as temperature, time and shear that are optimized for effective W/Og formation may differ from those for oleogel formation, resulting in divergent end-product characteristics. Finally, compared to O/W emulsions, the ability to enhance the functionality of W/Og systems is limited by the general lack of available oil-soluble emulsifiers and gelling agents.

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Ultimately, the ability to determine the contributions of the oleogel matrix, emulsifier, and dispersed aqueous phase to the structure, rheology, and shelf life of W/Og systems will result in their incorporation into novel food applications. Examples include reduction or removal of solid fat in processed foods such as sausages, pâtés, and chocolate. In such products, while targeting calorie or fat reduction and perhaps costs savings, maintaining textural and sensory attributes similar to their higher solid fat equivalents will be the prime consideration in order to meet consumer expectations. The successful introduction of a W/Og system into a processed food product will very likely hinge on controlling non-specific interactions with other added ingredients, which may affect stability and shelf life. For example, presence of proteins dissolved within the dispersed aqueous phase may hamper the ability of W/Og systems to effectively form whereas added salts may enhance the interfacial modulus of the oil-water interface. Such challenges demonstrate that a holistic approach that takes into consideration an entire product formulation rather than a model formulation is necessary for the successful design and use of W/Og systems in foods.

## AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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