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Structured Emulsions and Edible Oleogels as Solutions to *Trans* Fat

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Introduction and Recent Progress in Regards to *Trans* Fat Reduction

Trans fatty acids (TFAs) were created and used by industry to fill a demand for functional fats that were solid at room temperature and could withstand the oxidation stresses provided by temperatures in excess of 160 °C when frying (Kodali, 2005). By simply changing the configuration of an unsaturation from *cis* to *trans*, a greater ease of packing can be achieved, due to more symmetrical molecules. This creates a corresponding increase in the melting points of these fatty acids and increases their stability when subjected to high temperatures (Kodali, 2005). When greater functionality was combined with what were believed to be health improvements over saturated fat, the widespread use of *trans* fats seemed to be ensured. Many years later, the shocking truth about *trans* fat and its deleterious effects on cardiovascular disease were reported (Judd et al., 1994; Mensink and Katan, 1990; Willet et al., 1993). In 2006, mandatory labeling of TFAs became a requirement in the United States, in an attempt to force producers to reformulate products and reduce our consumption of these harmful fatty acids (U.S. Food and Drug Administration, 2012).

In December 2009, Health Canada released its final monitoring report that reported the level of TFAs in certain Canadian foods, including French fries, desserts, cookies, frozen appetizers, popcorn and snacks, and chicken products (Health Canada, 2012). The results were rather shocking, with only 4 of the 21 different product types tested meeting the required *trans* fat level. Only 40% of cookies from small- and medium-sized family and quick service restaurants met the requirements, and only 25% of margarines from cafeterias located in institutions met the *trans* requirements. Although 18 of the 21 categories had 50% or more of the tested products meet the necessary requirements, *trans* fats clearly remain a problem (Health Canada, 2012). It is possible that for many of these products the producers were unable to effectively replace *trans* fats with a substitute, either due to lack of availability, poor functionality on the substitutes' part, or cost.

The small change in unsaturated fatty acid bond configuration from *cis* to *trans* has represented a large problem to the food industry with regards to its replacement.

This created a great challenge for both academic and industrial scientists: Provide a solid-like structure similar to highly saturated or *trans*-containing triacylglycerols, keeping functionality, yet without having negative impacts on human health. Other additional factors such as cost, availability, versatility, efficiency, and food-grade status should also be considered when trying to find a replacement for *trans* fats (Co and Marangoni, 2012). A distinction can be made here: Replacements that fulfill only some of these requirements should be considered as "substitutes," while those that fulfill all of these requirements, and potentially provide additional benefits, can be deemed "solutions" to *trans* fats. Many previously proposed substitutes for TFAs have found their way into our diets. Their effectiveness as a solution to the issue can now be seen, well over five years after January 1, 2006, which was when the new labeling requirements were put into place (U.S. Food and Drug Administration, 2012). This chapter focuses on structured emulsions and edible oleogels, two potential solutions to the *trans* fat dilemma. However, to understand why these are potential solutions, background information in regard to how specific fatty acids affect our cardiovascular health is required.

Effects of Specific Fatty Acids on Our Cardiovascular Health

Cardiovascular disease (CVD) continues to be the leading cause of death and disability in the world, resulting in an estimated 17.3 million deaths in 2008, and a predicted 23.6 million deaths in 2030 (WHO, 2012). Blood serum cholesterol levels have been used for many years as an indicator for cardiovascular health, as a strong correlation was seen between high total serum cholesterol levels and CVD (Klag et al., 1993; LaRosa et al., 1990). Today, many different types of serum cholesterol have been identified, including the following: high-density lipoprotein (HDL), low-density lipoprotein (LDL), intermediate-density lipoprotein, very-low-density lipoprotein, and chylomicrons (LaRosa et al., 1990; Nordestgaard and Tybjærg-Hansen, 1992). Of these different types of lipoprotein, LDL and HDL are by far the most utilized to report effects on cardiovascular health, with increased LDL levels having a negative effect and increased HDL levels having a positive effect on cardiovascular health compared to baseline levels (LaRosa et al., 1990). Typically, serum cholesterol levels are measured after the consumption of meals or diets containing a specific amount and type of fat or fatty acid. These levels are then compared to a control meal or diet, which is often carbohydrates or one specific fatty acid, such as oleic acid. The work of Mensink and Katan (1990) was one such study that used oleic acid in their control diet, providing 10% of the subject's daily energy.

Although many studies in the 1990s looked only at total changes in serum cholesterol levels, or change in LDL, it has since been shown that it is much more advantageous to report both the change in LDL and HDL, or more specifically, as

a cholesterol ratio, ΔTotal:HDL (Mensink et al., 2003). The ratio is determined by adding the change for both LDL and HDL cholesterol, and comparing this to the change in HDL only. If the reported ratio is positive or close to 0, this means that there was primarily an increase in LDL levels, while a negative ratio indicates a larger increase in HDL relative to LDL. With this ratio, it is very clear what specifically increased, and whether this indicates a negative, neutral, or positive effect on CVD. The work of Mensink et al. in 2003 showed *cis*-polyunsaturated fatty acids had the greatest positive effect on CVD, with a ΔTotal:HDL ratio of approximately –0.032, while TFAs showed the worst effect, resulting in a ratio of just over 0.02 (Mensink et al., 2003). Saturated fatty acids showed a fairly neutral effect on the ΔTotal:HDL cholesterol ratio, while *cis*-monounsaturated fatty acids showed a ratio of –0.026, also indicating a positive effect on cardiovascular health (Mensink et al., 2003).

TFAs are considered to be the most deleterious type of fatty acids, predominately due to their effect on this cholesterol ratio. While TFAs caused the greatest increase in LDL levels, it was also the only type of fatty acid to decrease HDL levels (Mensink et al., 2003). This has been confirmed by many other groups, including Mozaffarian and Clarke (2009). This group also showed impact on the ΔTotal:HDL ratio if TFAs replaced poly, mono, or saturated fatty acids, on a basis of percent of calories replaced by *trans* fat. At the level of 1% replacement of calories, the values are very similar to the 0.02 reported by Mensink et al. (2003). However, when *trans* fat replaces 5% of calories formerly provided by polyunsaturated fatty acids, this value jumps to above 0.3, more than a tenfold increase (Mozaffarian and Clarke, 2009). When *trans* fat replaced 5% of calories from monounsaturated and saturated fat, the ratios were approximately 0.27 and 0.17, respectively (Mozaffarian and Clarke, 2009).

As with cholesterol, the general term "saturated fat" can be broken down into specific fatty acids, with two of the most heavily studied and prevalent in edible fats and oils being palmitic acid (C16) and stearic acid (C18). The effects of these fatty acids on serum cholesterol have been shown to be significantly different, and they should not be grouped together (Mensink et al., 2003). Stearic acid, which has been estimated to make up 3% of daily energy in the average American diet, has a slightly beneficial effect on serum cholesterol levels, with a ratio of –0.013 in the Mensink et al. (2003) study (Hunter et al., 2010). Palmitic acid shows a more negative effect on cardiovascular health, with a ΔTotal:HDL ratio of 0.005, and was the most atherogenic saturated fatty acid studied (ΔTotal:HDL). This is troubling because palmitic acid is the most heavily consumed saturated fatty acid in the United States, making up 56.3% of total saturated fat intake and resulting in 1.8–4.4% of daily energy for 14 European countries (Hunter et al., 2010).

Recently, the true effect of saturated fatty acids on human health has come under debate (Siri-Tarino et al., 2010a, 2010b). Contrary to what serum cholesterol values may indicate, a meta-analysis study covering close to 350,000 subjects found no

relationship between saturated fat consumption and increased risk of stroke or CVD (Siri-Tarino et al., 2010a). Although saturated fat may not be as damaging to health as once previously believed, it can still be concluded that saturated fats, individually or as a whole, do not have the same positive benefits that mono- and especially polyunsaturated fatty acids possess. When replacing 1% of energy formerly held by stearic acid with mono- or polyunsaturated fatty acids, ΔTotal:HDL cholesterol can be lowered by 0.043 and 0.055, respectively (Hunter et al., 2010). An overwhelming amount of evidence has shown that polyunsaturated fatty acids possess the greatest cholesterol lowering effects of all other types of fatty acids (Hunter et al., 2010; Kris-Etherton et al., 2004; Mensink et al., 2003). Many oils from vegetable sources contain a high percentage of polyunsaturates, as shown in Table 10-A. For the development of any solutions to *trans* fat, the inclusion of a high level of polyunsaturates should be a priority, while minimizing the level of saturated fat. Both edible oleogels and structured emulsions have the potential to take advantage of polyunsaturated fatty acids, while possessing highly reduced levels of saturates and zero TFAs. Although either of these fairly new approaches for creating a solid-like fat can achieve a goal of zero *trans* fat, each has its own set of advantages and specific applications.

Structured Emulsions Using Monoglycerides

Emulsions consist of at least two immiscible phases, with one phase being dispersed in the other as tiny droplets (McClements, 2010). The most common type of emulsion is oil in water (O/W), with some examples including milk, cream, and mayonnaise (McClements, 2010). It can be a challenge trying to differentiate between a structured emulsion, and a simple O/W or water-in-oil emulsion, as often they involve many of the same ingredients and production procedures. For example, both com-

Table 10.A. Fatty acid composition (wt%) of common fats and oils from vegetable sources

	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Oil Type	C12	C14	C16	C18	C18:1	C18:2	C18:3
Palm	—	2	44	4	39	11	—
Olive	—	—	13	3	75	8	1
Canola	—	—	5	2	62	21	10
Soybean	—	—	12	4	23	54	7
Corn	—	—	11	2	26	60	1
Flaxseed	—	—	6	4	15	16	59

Gunstone and Harwood (2007).

monly rely on a mixing or homogenization step to disperse one phase into the other, and they both commonly use a minute amount of emulsifier to help stabilize the emulsion (McClements, 2010). Traditional emulsions are prone to physical instability (coalescence and phase separation) and are not able to provide a solid-like texture that is similar to hard-stock triacylglycerol molecules (McClements, 2010). Although mayonnaise certainly has structure, it is unlikely that it would ever be described as looking "shortening-like." With structured emulsions, products with a wide variety of textures can be created, including something that is similar to a traditional partially hydrogenated shortening (Batte et al., 2007a; Zetzl and Marangoni, 2011). Several varieties of structured emulsions have been listed in a review by McClements (2010) and include the following: multiple emulsions, solid lipid particles, filled hydrogel particles, and multilayer emulsions. Here the focus will be on one variety of multilayer emulsions, as described by Marangoni (2007), which use monoglycerides to entrap multiple layers of water around oil droplets (Marangoni, 2007; Marangoni et al., 2007).

To understand more about this system, it is first important to describe how this type of emulsion is produced. The system can be created by first heating a cosurfactant-saturated monoglyceride–oil mixture above the Krafft temperature of the monoglycerides until they have become fully dissolved in the oil. This mixture is then added to water while briefly exposing the system to a gentle external shear field. This leads to the formation of a multilayer lamellar monoglyceride structure in the liquid crystalline state, which surrounds the oil droplets. Upon cooling below the Kraft temperature, the monoglycerides undergo a liquid-crystalline to crystalline phase transition and adopt a solid-like structure (Batte et al., 2007a, 2007b). The final product contains vegetable oil "droplets" surrounded by the hydrated, saturated, monoglyceride multilayers (Batte et al., 2007a; Marangoni et al., 2008; Zetzl and Marangoni, 2011). These droplets can be easily observed when using freeze fracture cryo-scanning electron microscopy, as shown in Figure 10.1 (A and B). By making adjustments regarding the charged cosurfactant ratio and/or pH, a semisolid material of high viscosity, similar to a shortening in appearance, can be formed (Batte et al., 2007a). Structured emulsions such as those mentioned here are already commercially available. One such product has been trademarked under the name Coasun™. This shortening-like material contains no TFAs, limited saturated fatty acids, and is 30–40% structured water (Figure 10.1C) (Zetzl and Marangoni, 2011).

The structure from the term *structured emulsion* comes from the monoglycerides, which are only incorporated at a level of a few percent, yet are able to stabilize the emulsion, greatly reducing phase separation and providing structure. In fact, the monoglycerides could potentially be the only actual solid component in these structured emulsions at room temperature. This structure can be seen when analyzing X-ray diffraction spectra in the small angle region, where the structured emulsion

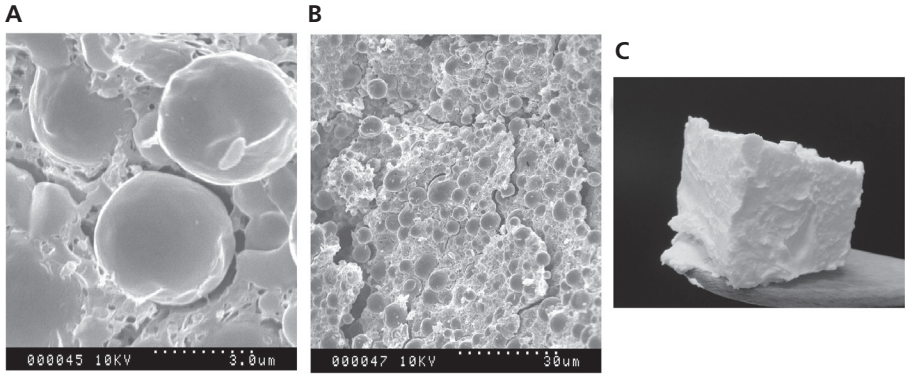
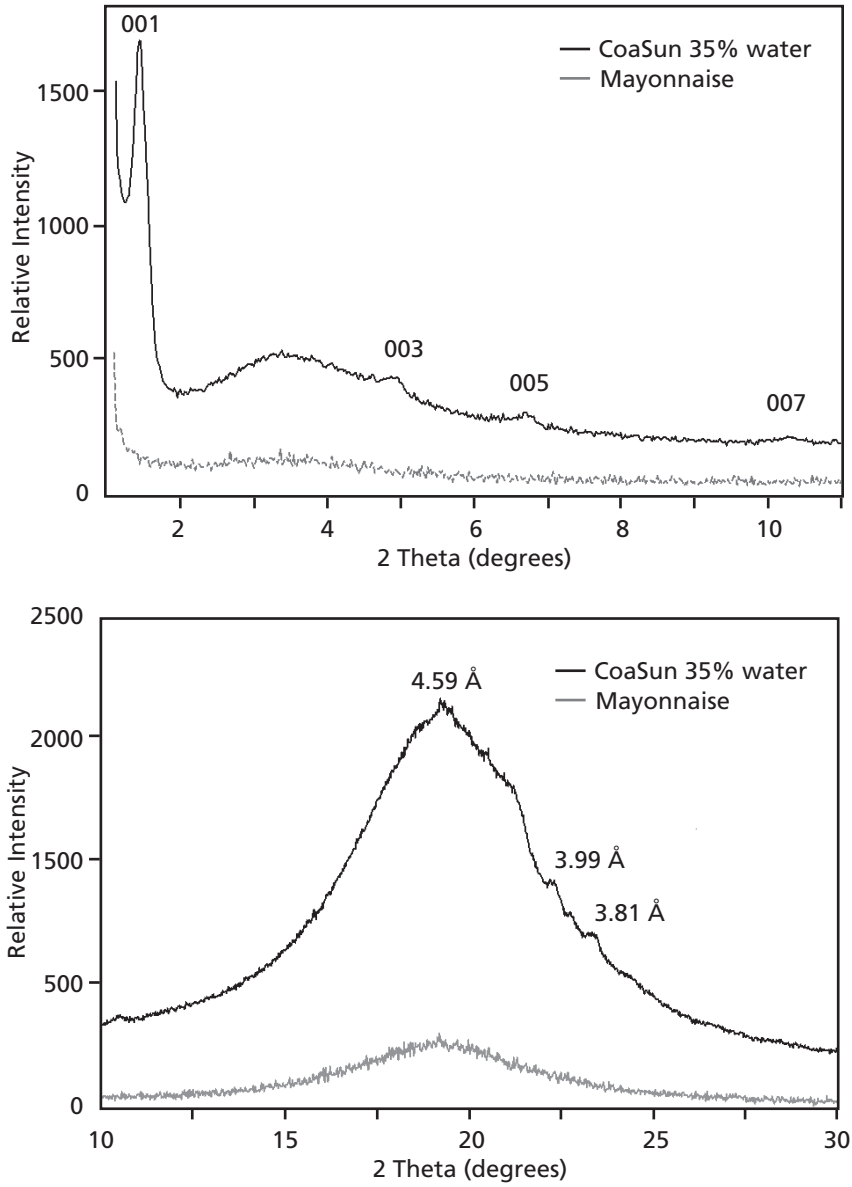


Figure 10.1 (A, B) Cryo-scanning electron micrographs of a structured oil-in-water emulsion, similar to the commercial product Coasun™. (C) Structured emulsion Coasun™, which can possess a shortening-like texture through the use of a surfactant and careful control of pH. Coasun™ can successfully be used for a variety of baking applications by replacing traditional fats high in saturated and TFAs.

(4.5% monoglyceride and 35% water) will show diffraction peaks (001, 003, 005, 007), yet mayonnaise will not (Figure 10.2). These peaks, which signify sizes of approximately 61 Å, 18 Å, 13 Å, and 8 Å for 001, 003, 005, and 007, respectively, indicate that there is a lamellar crystalline structure in the long spacing that is not shown by a traditional O/W emulsion, such as mayonnaise. Three definitive peaks were also noted in the wide angle region for the structured emulsion sample, whereas the mayonnaise emulsion showed no definitive peaks. Peaks in this region signify that there is subcell packing; specifically, the peaks indicate that the sample had converted from the metastable α-form to the more stable β-form.

Rheology can also be used to show the difference between an O/W emulsion (mayonnaise) and a structured emulsion (Coasun™), as shown in Figure 10.3. When analyzing the storage modulus (G') for the two different types of emulsions, at 10 Pa the structured emulsion has a G' of 3022 Pa, which is more than six times that of mayonnaise (461 Pa). This indicates a material that is stiffer and more solid-like, which might be unexpected considering that the Coasun™ product contains an additional 15% water compared to the mayonnaise. The differences in the loss modulus (G") is also quite substantial, with the structured emulsion showing a loss modulus over seven times that of mayonnaise (424 vs. 59 Pa).

Work was completed by Huschka et al. (2011) in an attempt to determine how similar this type of structured emulsion would behave to an actual interesterified vegetable shortening. The doughs containing structured emulsion showed a lower



Au: Theta spelled out ok here?

Figure 10.2 Small and wide angle X-ray diffraction spectra for Coasun™ and mayonnaise.

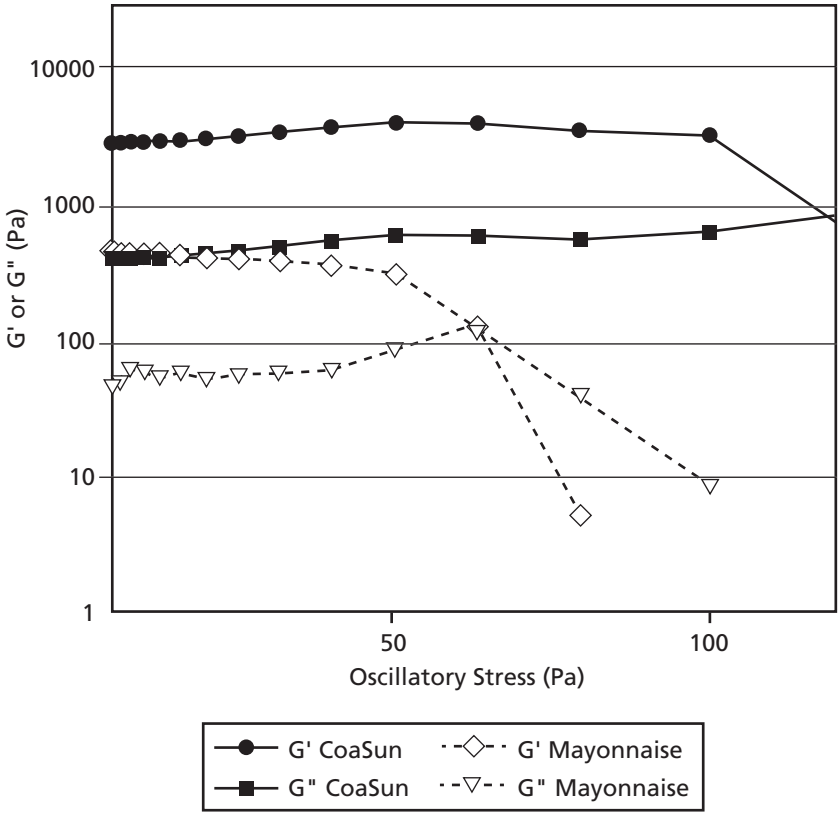


Figure 10.3 Storage modulus (G') and loss modulus (G") for the structured emulsion Coasun™ and a typical oil-in-water emulsion, mayonnaise, over a range of oscillatory stresses.

amount of water absorption compared to all other samples, including the interesterified soy oil, at lipid contents above 6%. This suggests the formation of a softer dough that had been "shortened." This prevention of cross-linkages between gluten molecules was especially noticeable in the dough samples using hard wheat flower, which contains a higher protein (gluten) content compared to soft wheat flower. Preventing gluten aggregation through the use of shortenings is beneficial for baked products that are not reliant on gluten for structure, such as cakes and tarts (Huschka et al., 2011). Based on these results, it is likely that a structured emulsion (Coasun™) could pose as a viable substitute for highly saturated and TFA-rich shortenings in these types of products. The same ingredients used in Coasun™, although not heated and

mixed together, were used as a control and did not demonstrate these same shortening properties, signifying the importance of the specific structure of these emulsions rather than simply the presence of the ingredients (Huschka et al., 2011).

Other than a low saturated, and zero *trans* fat content, additional physiological benefits have been discovered after consuming these multilayer structured emulsions. The unique structure of Coasun™ also has shown the ability to help regulate blood lipid and insulin responses in humans and to lower postprandial triacylglycerol levels (Marangoni et al., 2007; Rush et al., 2009). Once again, these lowering effects were not demonstrated when the raw ingredients alone were consumed, or when the structure was destroyed by cooking (Rush et al., 2008). Furthermore, there is potential for nutraceuticals such as phytosterols, omega-3 fatty acids, fat soluble antioxidants, and other compounds (which will be discussed further later in this chapter) to be incorporated into the water or oil component of these structured emulsions as an added nutritional benefit (Zetzl and Marangoni, 2011).

Due to the increased incorporation level of water, the final product is fairly inexpensive, especially when its multitude of potential health benefits are taken into consideration. Although continued research is required as to how these structured emulsions behave in food systems, they may be one of the best solutions to the *trans* fat dilemma, especially in the bakery industry where it's shortening-like structure would be ideally suited (Lin and Appleby, 2012).

Organogels

Organogels, also known as *oleogels,* can be defined as an organic liquid entrapped within a thermo-reversible, three-dimensional gel network (Zetzl and Marangoni, 2011). The process of forming an organogel is called *organogelation.* Molecules capable of forming nonpolar aggregated molecular or crystal networks, with the ability of entrapping or structuring oil, were certainly not unheard of in the scientific community and industry prior to the 1990s. However, it was not until the late 1990s that the potential for these molecules to be used as a vegetable oil structurant and food ingredient began to be realized (Co and Marangoni, 2012). As of 2012, there have been several reviews published regarding the many known organogelators, their properties, advantages, and disadvantages (Bot et al., 2009; Co and Marangoni, 2012; Pernetti et al., 2007a; Rogers, 2009).

The following are general categories of network-forming edible oil structurants that have been identified: monoacylglycerols (MAGs), fatty acids, fatty alcohols, waxes, wax esters, sorbitan monostearate. lecithin and sorbitan tri-stearate, and phytosterols and oryzanol (Pernetti et al., 2007a). In addition, the following organogelators or mixtures thereof are well known for having an ability to structure edible oils: 12-hydroxystearic acid (Rogers and Marangoni, 2008; Rogers et al., 2007,

2008; Terech and Weiss, 1997), ricinelaidic acid (Wright and Marangoni, 2006), candelilla wax (Toro-Vazquez et al., 2007), rice bran wax (Dassanayake et al., 2009), sunflower wax (and other waxes) in soybean oil (Hwang et al., 2012), several waxes in canola oil (Blake and Marangoni, 2013), mixtures of β-sitosterol and γ-oryzanol (Bot and Agterof, 2006), mixtures of stearic acid and stearyl alcohol (Gandolfo et al., 2003), mixtures of lecithin and sorbitan tri-stearate (Pernetti et al., 2007b), and more recently, mixed ceramides and ethylcellulose (Rogers, 2011; Zetzl et al., 2012).

Waxes and Wax Organogels

For decades waxes have played an important part outside of the food industry. A wax can be defined as a fatty substance that contains long hydrocarbon chains with or without a functional group (Dassanayake et al., 2011). It is unknown as to how far back their uses go, but the oil structuring ability and texture they provide to products such as lipstick, lip balms, and lotion bars are necessities (Toro-Vazquez et al., 2007). Previously, to structure oil effectively, waxes had to be used at levels close to or in excess of 5%, making them impractical for most food uses because they would impart a waxy mouthfeel. Carnauba wax, for example, is only able to structure oil at levels in excess of 4% (Dassanayake et al., 2009). More recent studies have shown the superior oil-binding ability of certain waxes that are able to gel oil at levels as low as 1% (Blake and Marangoni, 2013; Dassanayake et al., 2011; Toro-Vazquez et al., 2007, 2011). With wax incorporation levels of only a few percent of the fat phase, this may provide a texture and mouthfeel that is more acceptable to consumers.

Candelilla wax is one such wax that shows great potential as an organogelator. Obtained from the leaves of a small shrub native to the southern United States and northern Mexico, candelilla wax consists of 49–50% n-alkanes with 29 to 33 carbons, and 20–29% esters of acids and alcohols with 28 to 34 carbons (Toro-Vazquez et al., 2007, 2011). Candelilla wax has been shown to structure safflower oil at levels as low as 1%, while actual gelation was not found to occur until concentrations were raised to 2% (Toro-Vazquez et al., 2007, 2011). This wax appears to be limited by the type of crystals it forms, which are usually less than 10 μm in size and spherulitic in shape (Toro-Vazquez et al., 2011). To effectively entrap oil, much longer and thinner crystals, such as those formed when using rice bran wax, are usually needed (Co and Marangoni, 2012). Wax derived from rice (*Oryza sativa)* bran possesses long needle-like crystals in oil, ranging from 20 to 50 μm, that are very effective in entrapping oil within a crystalline matrix (Co and Marangoni, 2012; Dassanayake et al., 2011). These crystalline strands are so effective, in fact, that they have been shown to gel oil as low as 1% w/w (Blake and Marangoni, 2013).

With the large production levels of rice in eastern Asia, rice bran wax is very inexpensive, and was traditionally considered a waste product of the rice milling

process (Dassanayake et al., 2011). This means that it is largely available, and cost effective, with the possibility to greatly reduce the amount of saturated fatty acids while eliminating any TFAs. Unfortunately, gels containing only 1% wax are very soft and have an oily appearance. It is probable that much higher levels would have to be used to produce a fat that is similar to lard or shortening in texture. At such a high incorporation level, it is unknown as to how noticeable and waxy the mouthfeel of the fat would be, which would have a negative effect in regards to consumer perception.

In Figure 10.4, the structure of the aforementioned wax oleogels can be seen at a wax incorporation level of 10% (w/w) in canola oil. These images give a better understanding as to why rice bran wax is able to gel oil at the lowest concentration compared to the other two waxes. Carnauba wax, the wax with the highest critical gelator concentration, formed large, open, dendritic clusters or aggregates, which are

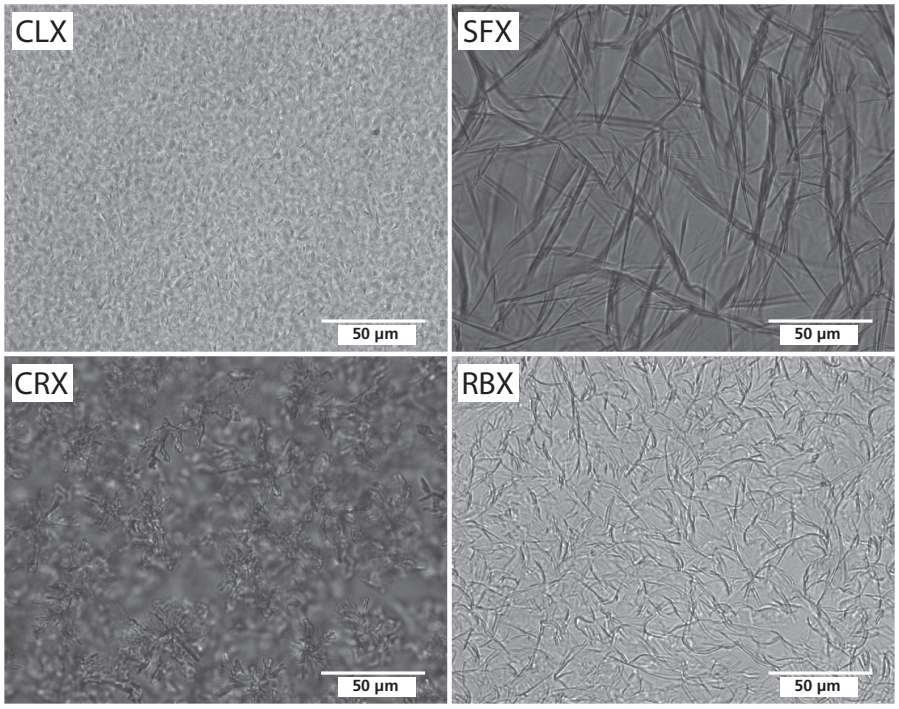


Figure 10.4 Brightfield light micrographs of wax–oil gels consisting of 10% wax (w/w) in canola oil at a temperature of 25 °C. The different waxes are labeled as follows: candelilla wax (CLX), carnauba wax (CRX), sunflower wax (SFX), and rice bran wax (RBX).

not very effective in entrapping oil. Although the structure of candelilla wax is better for gelling oil compared to carnauba wax, it is only rice bran wax out of the three that forms very long, needle-like crystals that are very effective in forming gels (Blake and Marangoni, 2013; Co and Marangoni, 2012).

Sunflower wax, derived from sunflower seeds, has barely been mentioned in literature compared to these three other waxes, yet it may provide oil-binding properties that are similar or even superior to rice bran wax (Blake and Marangoni, 2013; Hwang et al., 2012). As can be seen in Figure 10.4, sunflower wax has formed crystals that are in excess of 100 μm, which allows for more junction zones to be formed along each crystal strand and increases the strength of the gel network (Blake and Marangoni, 2013; Hwang et al., 2012). Compositional purity has also been shown to have an effect on wax gelation. Minor components in the waxes have the potential to act as impurities, impairing gelation and changing morphology in regard to crystal size and potentially shape (Blake and Marangoni, 2013). While rice bran wax consists of over 90% esters, sunflower wax contains 97–100% esters and contains the fewest minor components out of the four aforementioned waxes (Blake and Marangoni, 2013). This high level of compositional purity also aids in the understanding as to why rice bran and sunflower wax are such good organogelators in comparison to other waxes. Although low critical gelator concentrations can be achieved when using these two waxes, it seems that their ability to hold the oil in its gel state is fairly low, with the percent oil loss exceeding 50% when gels were made with 1% wax (w/w). Oil loss was measured by placing gel samples inside a glass funnel lined with Whatman #5 filter paper and measuring the amount of oil collected in a beaker below the funnel for 24 hours. In comparison, candelilla wax showed only a 25.8% oil loss at the 1% (w/w) incorporation level, and only 11.1% oil loss at the 2% (w/w) incorporation level (Blake and Marangoni, 2013). Although oil loss values are dependent on the test conditions, these differences show that there are a variety of factors that should be taken into consideration when choosing a wax for organogelation purposes, not just the critical gelation concentration.

Clearly there is great potential in the field of waxes to structure oils, although many questions still remain, especially in regard to how these gels will behave in food systems. Although they have the possibility to become a substitute or solution to TFAs in the future, a significant amount of research and development must still take place in this field.

Oleogels Made Using 12-Hydroxystearic Acid

Similar to waxes, the low molecular weight organogelator 12-hydroxystearic acid (12-HSA) also has the ability to gel vegetable oil at levels below 2% (w/w) (Hughes et al., 2011). This molecule is derived from castor oil, and has been used for decades by

industry in the production of lithium grease (Co and Marangoni, 2012). Structurally, 12-HSA is 18 carbons long and possesses a hydroxyl group at position 12 (Rogers and Marangoni, 2011). Oleogels are formed by heating the 12-HSA-in-oil mixture to above the melting point of the 12-HSA, which occurs at approximately 76 °C (Co and Marangoni, 2012). Upon cooling, 12-HSA fibers form throughout the oil, growing one dimensionally to hundreds of micrometers in length. In Figure 10.5, a bright to dark striation pattern can be seen on each of these fibrillar crystals. This is the result of a helical twist of the 12-HSA fibers, causing them to pass in and out of birefringence under polarized light (Co and Marangoni, 2012; Rogers and Marangoni, 2011). An extensive characterization of these oleogels has been previously described by Rogers and Marangoni (2011) and Co and Marangoni (2012), though it is perhaps the health implications of consuming such an oleogel that are of greatest interest to the food industry.

A review chapter by Hughes et al. (2011) reported the results of a clinical trial reported in which subjects were fed standardized test meals that differed only by the fat source they contained, which were butter, margarine, canola oil, or gelled canola oil (using 12-HSA) (Hughes et al., 2011). After consumption of the test meals, blood samples were taken every hour for six hours and were analyzed for triacylglycerols, free fatty acids, glucose, and insulin levels. No significant differences were found between the treatments in regard to glucose or insulin levels; however, the oleogel and canola oil meals significantly reduced the serum triacylglycerol response curves, compared

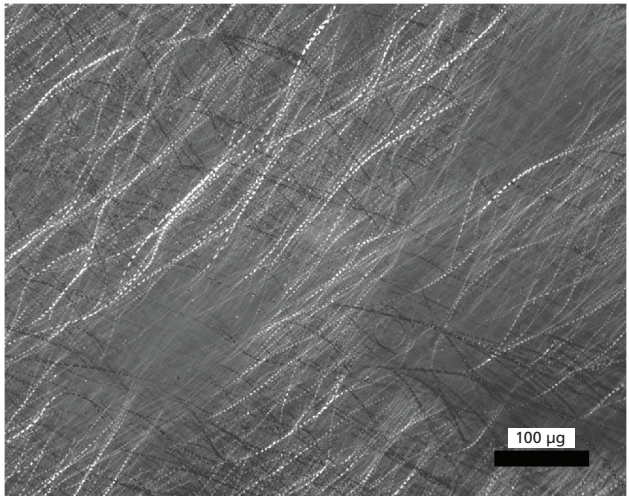


Figure 10.5 A polarized light micrograph showing the fibrillar crystals of 12-hydroxystearic acid in canola oil at a concentration of 2.5% (w/w).

to those from the margarine and butter meals, for the majority of the measurements (Hughes et al., 2011). The oil gelled with 2% w/w 12-HSA also showed the lowest maximum serum free fatty acid levels compared to all other meals (though it was not significantly less than the meal containing canola oil) (Hughes et al., 2011). These effects are added benefits that go beyond the fatty acid compositional benefits provided by all oleogels made with a high percentage of vegetable oil. Although this study utilized 12-HSA, it is possible that, if consumed in a similar manner, oleogels made using other oraganogelators could show similar beneficial physiological effects.

While 12-HSA is an exceptional organogelator, it unfortunately does not currently have full food-grade status (Co and Marangoni, 2012). In addition, for any food systems in which the shearing or mixing of these oleogels would be required, the use of 12-HSA as the organogelator would not be possible because the long fibrillar crystals are very delicate and essentially shatter under these conditions. This damage to the fibrillar network is nonrecoverable and results in a high percentage of oil loss. It is therefore likely that while oleogels show a great deal of potential in food systems, it is probable that other organogelators, such as polymers, will be used in place of the fibrillar network forming 12-HSA.

Ethylcellulose (Polymer) Oleogels

For the purposes of creating a food-grade oleogel, the use of a polymer such as ethylcellulose (EC) is highly novel, although this is rather surprising considering that its solubility properties were reported as early as 1937. The work of W. Koch stated that "solubility in both polar and nonpolar organic solvents is best with ethylcellulose of substitutions between 2.4 and 2.5 ethoxy groups" (Koch, 1937). At the time, this must have seemed like a trivial detail; however, this means that EC can be used as an organogelator of food-grade oils, as a common vegetable oil would classify as a nonpolar solvent. It is likely that this detail was originally simply overlooked, as there was no need to create a substitute for *trans* or saturated fats. Not until the past decade has the potential of oleogels, and in particular polymer oleogels, become fully realized. Figure 10.6A shows an example of a firm and stable oleogel made using only soybean oil and ethylcellulose, while 10.6B shows a laminate-type pastry where an oleogel replaced 50% of the traditionally used fat (discussed further in the "Production Considerations and Food Applications of Ethylcellulose Oleogels" section).

Ethylcellulose is a chemically modified version of the plant cell wall–based polymer cellulose. Ethylcellulose differs from cellulose only by the substitution of hydroxyl groups for ethoxyl groups, with a maximum of three substitutions possible. Solubility in water is achieved when the average substitution is between 1 and 1.5, while only in the narrow range of 2.4–2.5 substitutions, 47–48% ethoxy content, is solubility in oil possible (Zetzl and Marangoni, 2011; Zetzl et al., 2012). Though solubility in

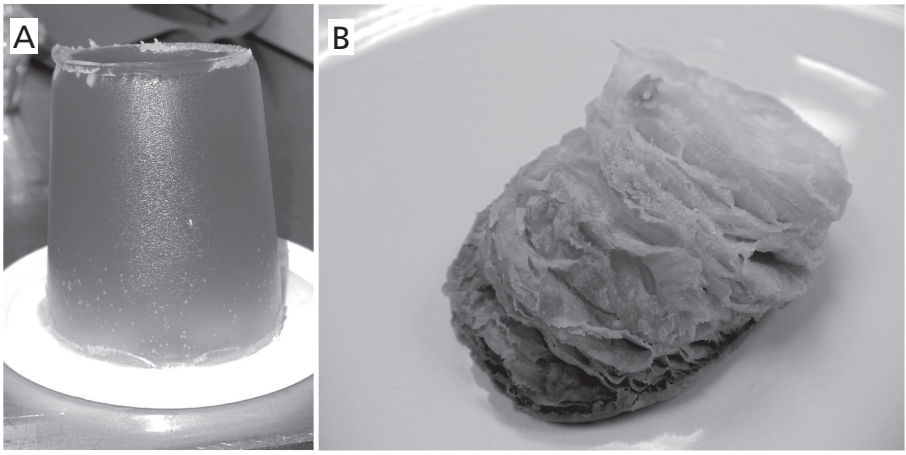


Figure 10.6 (A) Ethylcellulose oleogel consisting of 10% 45 cP ethylcellulose (w/w) and 90% soybean oil. The oleogel remains stable and is very solid at room temperature. (B) A laminate type pastry made with a 50% substitution of butter with an ethylcellulose oleogel.

oil was not a requirement of the commercial product, the 2.4–2.5 substitution level has been the standard substitution level used by industry since the 1930s. Compared to organogelators used in the past, ethylcellulose is rather inexpensive and can be produced (and purchased) in large volumes. This makes the large-scale use of EC for organogelation both possible and feasible.

For solubility in oil to occur, the ethylcellulose must be heated above the glass transition temperature (T_g), which occurs at approximately 130 °C. A variety of molecular weights are available, expressed as a cP value, with 10–100 cP being the range that is most practical for organogelation purposes. Molecular weights can be calculated, but they are not provided by ethylcellulose suppliers (Zetzl et al., 2012). Table 10-B shows the melting point, as well as the onset, midpoint, and final temperature for the glass transition of three varieties of ethylcellulose, in addition to the matching cP values and calculated molecular weights. Figure 10.7 shows a sample differential scanning thermograph of 10, 45, and 100 cP ethylcellulose powder, which can be used to determine the T_g and melting point of the polymer. Though it is only the T_g that is needed to create a gel, the melting point for these varieties is useful information because at temperatures above this point it is highly likely that the polymer will begin to break down or degrade. By remaining within the functional range between the T_g and the melting temperature, the quality of the EC can be preserved while retaining its ability to make oleogels.

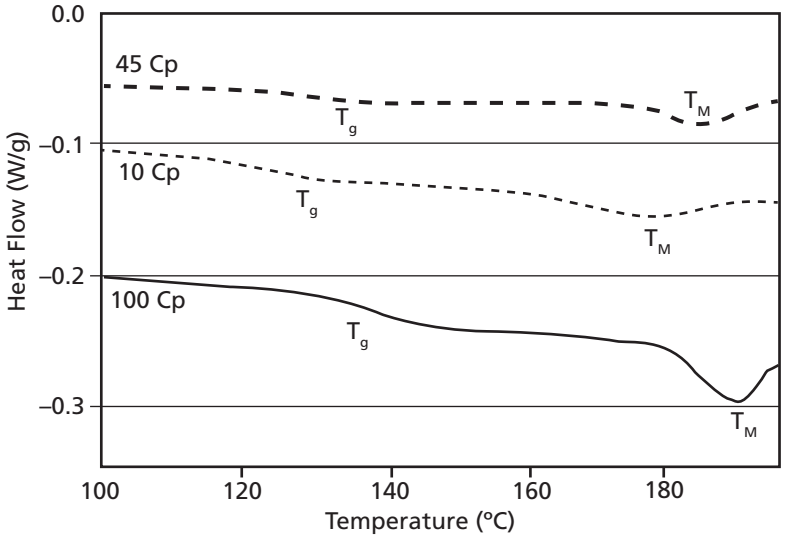


Figure 10.7 Sample differential scanning calorimetry thermogram showing the glass transition and melting for 10, 45, and 100 cP ethylcellulose powder.

A great deal is already known about the mechanical properties of EC oleogels. Recent studies have shown that the mechanical strength of these gels is highly dependant on the fatty acid composition of the vegetable oils used in making the gels (Figure 10.8) (Laredo et al., 2011; Zetzl et al., 2012). Oils such as canola, which contain a fairly low comparative degree of unsaturation (approximately 60% oleic acid, 18:1), produce fairly soft gels. Flaxseed oil, which contains close to 60% linolenic acid (18:3), produces substantially harder gels (Laredo et al., 2011; Zetzl et al., 2012). This increase in gel hardness corresponds to a statistically similar change in the elastic modulus of gel samples made with different vegetable oils. It is believed that these differences are caused by a change in the molar density of the oils within the gels. Essentially, oils with a higher degree of unsaturation are able to pack more tightly within the gel network, causing a firmer gel (Laredo et al., 2011; Zetzl et al., 2012). Even prior to gelation, a relationship can be seen regarding level of unsaturation and molar density. At 25 °C, canola oil has a density of 0.9134 g/cm^{-3}; soybean oil, 0.9167 g/cm^{-3}; and flaxseed oil, 0.9250 g/cm^{-3} (Laredo et al., 2011). Attenuated total internal reflection infrared spectroscopy has been used to look at the differences between these oils in their gelled state. As the level of unsaturation increased, so did the intensity ratio between the band at 3007 cm^{-1} (=C-H stretching) and 2870 cm^{-1} (CH_3 symmetric stretching). This signifies an increasing difference in the level of =C-H stretching between the gels and the pure oils as unsaturation increases (Laredo

Table 10.B Glass transition and melting temperatures for ethylcellulose powder of different molecular weights, determined using a TA Instruments Q1000 differential scanning colorimeter with a temperature ramp of 5 °C / min. Letters indicate significance at a confidence level of 95% for three replicates using a tukey post-test, while standard error is indicated after the ± symbol.

Ethylcellulose Viscosity[†]	10 cP	45 cP	100 cP
Ethylcellulose Molecular Weight*	24 kDa	57 kDa	74 kDa
T_g Onset Temperature	$125.0^{a} \pm 0.57$	$130.6^{ab} \pm 0.13$	$131.1^{b} \pm 2.02$
T_g Mid-Point Temperature (°C)	$131.0^{bde} \pm 0.15$	$137.8^{c} \pm 0.33$	$136.1^{cd} \pm 2.79$
T_g Final Temperature (°C)	$136.1^{ce} \pm 0.53$	$141.1^{cf} \pm 0.67$	$146.0^{f} \pm 0.05$
Melting Point (°C)	$178.8^{g} \pm 0.35$	$185.8^{h} \pm 0.36$	$188.2^{h} \pm 0.91$

[†]Determined by making a 5% solution of ethylcellulose in a solvent (80% toluene and 20% ethanol), and measuring at 25 °C in a rotational viscometer

*As calculated in Zetzl et al. (2012).

et al., 2011). In addition, Raman spectroscopy revealed a higher number of *gauche* conformers in the gels compared to the pure oils, with the fatty acid chains becoming more disordered or bent when they were in their gelled state (Laredo et al., 2011). This supports the hypothesis that the linolenic acid molecules in flaxseed oil are more tightly packed within the gel network compared to the oleic acid molecules in canola oil. It is possible that analysis of scanning electron and atomic force micrographs could provide additional evidence regarding the density of the gel network when using vegetable oils containing different unsaturation levels.

The effect of polymer molecular weight has also been shown to have a significant impact on the mechanical properties of these polymer oleogels. As previously mentioned, molecular weight is expressed as a cP value, with ethylcellulose of 10 cP possessing a lower molecular weight, on average, than 20, 45, or 100 cP. Increases in molecular weight have been shown to produce gels that were significantly harder than low molecular weight varieties (Figure 10.8). Compared to 10 cP, oleogels made with 45 cP are nearly 10 times harder, while gels made using 100 cP ethylcellulose are more than 20 times harder when using soybean oil (Zetzl et al., 2012). As higher molecular weight varieties of ethylcellulose would contain longer polymer chains, it is hypothesized that these longer chains would be able to form a higher number of junction zones, improving network strength.

Polymer concentration is one additional factor that has a very significant effect on gel strength. When using 45 cP ethylcellulose, critical gelator concentrations of 4% and 6% were determined when using soybean and canola oil, respectively (Zetzl et al., 2012). In addition, when the hardness values at different polymer concentrations were plotted, both canola oil and soybean oil followed a power-law function with a

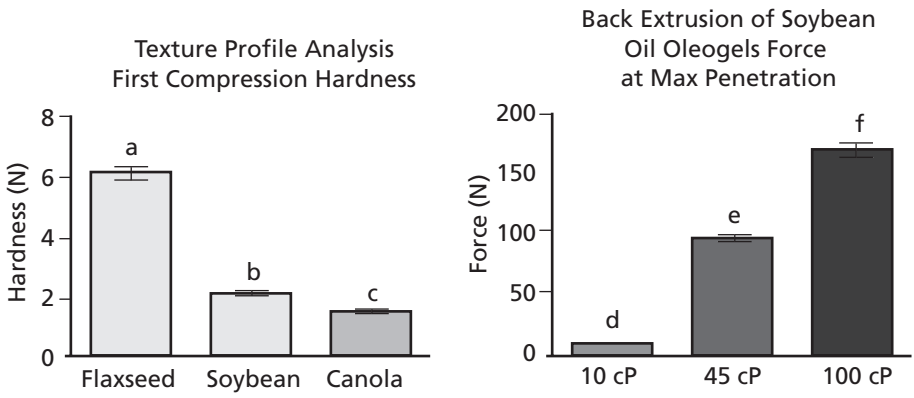


Figure 10.8 Texture profile analysis and back extrusion results for testing the mechanical properties of oleogels made with 10% ethylcellulose (w/w) in vegetable oil. The texture profile analysis results show the effect of oil type on hardness, while the back extrusion results illustrate the differences in hardness due to ethylcellulose molecular weight.

scaling factor of approximately 6, with an r^2 value of 0.99 (Zetzl et al., 2012). Using this data, it might be possible to predict the approximate hardness of gels made with a certain polymer concentration.

Imaging the Polymer Network Structure of Ethylcellulose Oleogels

Attempting to image the polymer network structure of a polymer oleogel such as this has posed a great challenge. Many organogelators display birefringence under polarized light, allowing networks or dispersions to be easily viewed using a polarized light microscope, as previously shown in Figure 10.5. When EC in water or oil is viewed under polarized light prior to heating, some birefringence can be observed, as shown in Figure 10.9A. Typically, a glass should not show any birefringence under polarized light; however, it appears that after the production process to the glassy state, crystallinity of some sort is still present in the ethylcellulose powder. This crystallinity can also be seen when using small angle X-ray scattering (SAXS), where 10 cP ethylcellulose powder produces a diffraction peak corresponding to a lattice parameter of 57.97 Å. Although a diffraction peak is seen in the SAXS region, there are no identifiable peaks in the wide angle region.

These results indicate that no crystalline packing of the ethylcellulose chains is occurring, yet it is possible that crystalline arrangements or bundles of ethylcellulose are forming, resulting in the diffraction peak in the small angle region. In cellulose,

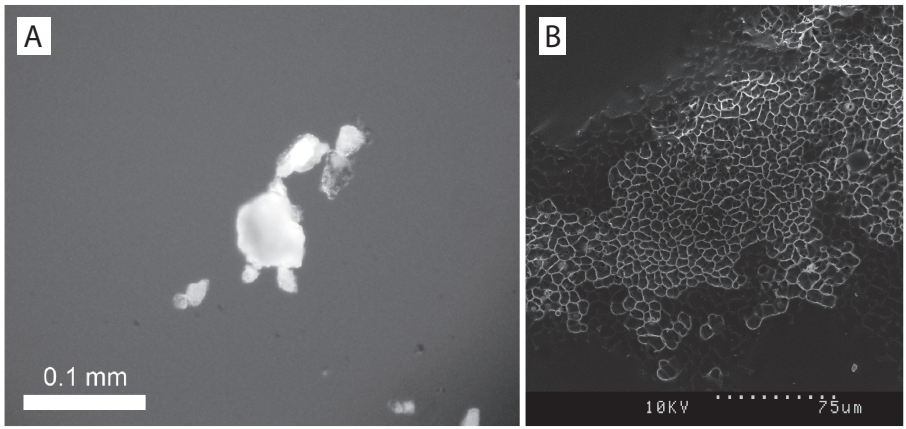


Figure 10.9 (A) Polarized light micrograph of 10 cP ethylcellulose powder in water. (B) A cryo-scanning electron micrograph of a canola oil organogel using 45 cP ethylcellulose, treated with 3.4 mL of isobutanol to remove surface oil.

individual cellulose chains interact via van der Waals and hydrogen bonding, forming microfibrils, which can be identified by a diffraction peak in the SAXS region (Müller et al., 1998). The exact position of the peak is highly variable, depending on the size and arrangement of the microfibrils, which is organism specific (Müller et al., 1998). The mean diameter of microfibrils has been shown to range from 25 to 200 Å, depending on the source of the cellulose (Müller et al., 1998). The 57.97 Å peak noted for ethylcellulose falls within this range and may indicate a similar grouping or bundling of ethylcellulose chains, which show birefringence under polarized light. After oleogels are made through heating of the ethylcellulose, any noted crystallinity disappears completely because birefringence is no longer seen under polarized light and no peaks are visible in the SAXS region. This means that techniques other than polarized light microscopy or powder XRD have to be utilized to try and view the microstructure of these polymer oleogels.

Preliminary images taken using cryo-scanning electron microscopy using a freeze-fracture technique also did not uncover many details in regard to the polymer network structure (Laredo et al., 2011). The work of Dey et al. (2011) also shows cryo-scanning electron micrographs of ethylcellulose oleogels. These researchers submerged 0.2 g gel samples into 40 mL of solvent in an attempt to expose a polymer network structure; however, yet again, few clear structures were discernible (Dey et al., 2011). Finally, in 2012, by using only a small amount of solvent in an attempt to wash away only oil at the surface of the oleogel, it was possible to uncover a view of the polymer network structure below, as shown in Figure 10.9B (Zetzl et al.,

2012). This image shows what is believed to be a continuous polymer network of ethylcellulose strands surrounding pores that would normally be filled with vegetable oil. Without the use of a solvent, the sample surface is completely smooth, as can be seen on the top and bottom portion of Figure 10.9B. Through the analysis of cryo-scanning electron micrographs, it is possible that these images may reveal further details regarding ethylcellulose oleogels, including a possible connection between gel microstructure and mechanical properties.

Production Considerations and Food Applications of Ethylcellulose Oleogels

On a slightly negative note, it appears that the preparation method used to produce ethylcellulose oleogels has a significant effect on gel properties, in particular, the number of oxidation products found in the sample (Gravelle et al., 2012). An increase in the thiobarbituric acid (TBA) value can be seen with extended holding time above the glass transition temperature (Gravelle et al., 2012). This value, along with the peroxide value, can give a good indication as to the level of oxidation in a vegetable oil. For canola oil oleogels, the TBA value increased from just over 0.08 to close to 0.13 after 90 minutes holding time above the T_g (Gravelle et al., 2012). The peroxide value of these gels also increased from approximately 2.5 meq/kg to approximately 14 meq/kg after 60 minutes (Gravelle et al., 2012). It was suggested that a holding time of 20 minutes should be used, as any longer and the oil quality would no longer be acceptable based on the peroxide values (Gravelle et al., 2012). In addition, an increase in the percent of total polar components was also noted as a function of holding time, increasing from 2.5% at 0 minutes to 4.0% and 6.5% after 60 and 120 minutes, respectively (Gravelle et al., 2012). The higher prevalence of these oxidation components caused a significant increase in the mechanical strength of the oleogels. It is believed that as the polarity of the oil increases, it is able to form hydrogen bonds to the ethylcellulose, helping to increase the strength of the gel network (Gravelle et al., 2012).

When heating a vegetable oil to temperatures in excess of 100 °C, oxidation will always be a factor. As previously mentioned, to produce these gels, a temperature in excess of 140 °C is required, which is above the glass transition temperature of the ethylcell ulose powder (~135 °C). This causes not only oxidation of the oil, but also has the potential to degrade any surfactants used, in addition to degrading of the polymer itself. It was, therefore, necessary to develop a standard procedure for the production of these gels, as described by Gravelle et al. (2012), to improve reproducibility and reduce oxidation. By combining this improved production method with an antioxidant such as butylated hydroxytoluene (BHT), it is likely that the overall acceptance of the produced oleogels in regards to palatability would be greatly improved.

Something unique about ethylcellulose oleogels compared to most other oleogels is that they have actually been used in real food systems as a replacement for more highly saturated animal fats. A number of recent studies have discussed potential applications of these gels, including their use in cookies, comminuted meat products, creams for various fillings (predominately baked goods), and chocolate (Stortz and Marangoni, 2011; Stortz et al., 2012; Zetzl et al., 2012). Figure 10.10 shows cooked ground and comminuted meat products that were made using 100% replacement of added animal fat with ethylcellulose oleogels. This replacement significantly reduced the amount of saturated fat in these products. While nongelled oil tends to leak out of the ground products, or make comminuted meat products significantly harder and chewier, gelling the oil prevents both of these problems. Oil is immobilized, and is not lost from breakfast sausages upon cutting, while cooked comminuted meat products made with gelled canola oil showed no significant differences in regard to chewiness and hardness when compared to a beef fat control product (Zetzl et al., 2012). This textural improvement compared to products made with nongelled oil appears to be caused by an increase in the size of the fat/oil globules in the cooked meat batter. As can be seen in Figure 10.11, the average fat globule size is greatly increased once the oil is in its gel form. Although these globules are still smaller than those found in the beef fat products, this increase in size still has a great impact on product texture. It is believed that the smaller globules in the canola oil product allow for a larger surface area to be coated by proteins, increasing the strength of the protein network (Zetzl et al., 2012).

Outside of meat systems, ethylcellulose oleogels have also very recently been used in the production of pastries, in particular, laminate type products that are notorious for being difficult to produce with any fat other than butter. The product shown in

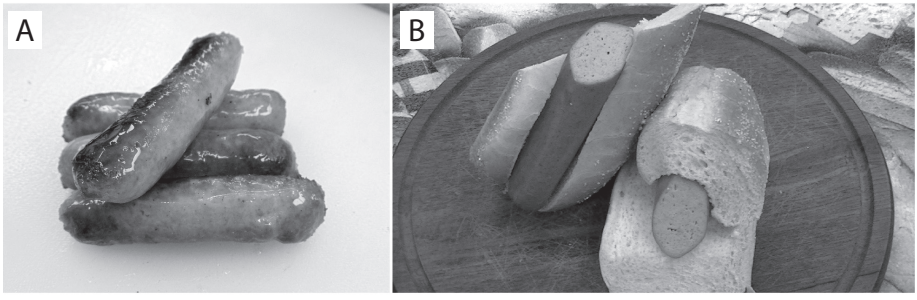


Figure 10.10 (A) Breakfast sausages (a ground meat product) and (B) frankfurters (a comminuted meat product) containing a 100% replacement of the traditionally added animal fat with an ethylcellulose oleogel.

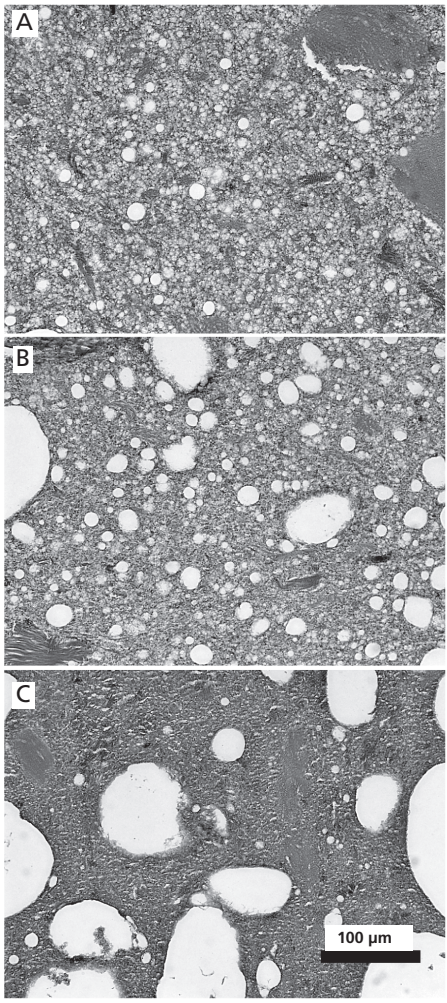


Figure 10.11 Cooked comminuted meat batter micrographs with various fat sources: (A) canola oil, (B) canola oil oleogel, and (C) beef fat. The white circular globules are fat globules (removed during the paraffin embedding process), while the dark surrounding area is the protein network in which some small intact muscle fibers still exist. The scale bar is the same for all three images, and is 100 µm.

Figure 10.6B contains a 50% replacement of butter with an ethylcellulose oleogel, significantly reducing the amount of saturated fat while still allowing the formation of lamination layers. Creams for the purpose of fillings in the baking industry can also be made using ethylcellulose oleogels, reducing oil migration from the filling into the surrounding product and also improving the fatty acid profile of the cream. Creams consisting of 60% gelled vegetable oil and 40% interesterified palm oil showed almost 0% oil leakage after 12 days, while creams made with nongelled oil showed close to 25% oil leakage (wt%/g sample) after 12 days (Stortz et al., 2012).

Although the primary focus of these replacement experiments was to reduce the amount of saturated fat while retaining functionality, it may be very possible to use ethylcellulose oleogels as a method to reduce *trans* fat in similar products. The baking industry in particular still has many items, including donuts, muffins, and cookies, that are high in saturated fat and still contain *trans* fat. If these gels are able to replace saturated fat in such a wide variety of products, while at the same time retaining product texture and palatability, it is possible they can be used in similar products to finally eliminate any *trans* fat they still contain.

In North America, ethylcellulose is currently approved for indirect food uses, such as use in inks to mark fruits and vegetables, and as a component of paper and paperboard that is in contact with fatty or water-based foods (Zetzl and Marangoni, 2011). In Europe, ethylcellulose has been approved for food uses since late 2006 (Zetzl and Marangoni, 2011). Internationally, the Food and Agriculture Organization of the United Nations, in collaboration with the World Health Organization, has listed ethylcellulose as a food additive that may be used in a variety of foods under the conditions of good manufacturing practices as outlined in the Preamble of the Codex GSFA (FAO and WHO, 2012). Some of the foods listed include processed comminuted meat, poultry and game products, fat spreads, fat emulsions, cheeses, bakery wares, and confectionery products (FAO and WHO, 2012). Although EC may not yet have full food-grade status worldwide, it is highly likely that such a development will occur in the near future.

Using Oleogels for Nutraceutical Delivery or Encapsulation

There have been recent discussions into how to make an oleogel, usually consisting of at least 90% vegetable oil, even healthier. One of the easiest ways to do so would be to use the oleogel to deliver lipid-soluble nutraceuticals. Nutraceuticals can be defined as "a food (or part of a food) that provides medical or health benefits, including the prevention and/or treatment of a disease" (Brower, 1998). For incorporation into an oleogel, it would be most advantageous to use a fairly purified compound because it would not be hindered or restricted by the food matrix where it was originally contained. Oil-soluble compounds such as omega-3 fatty acids, the carotenoids β-carotene and lycopene, phytosterols, coenzyme Q, and vitamin E have all been identified as potential compounds of interest for incorporation into oleogel systems (Zetzl and Marangoni, 2012). These compounds are discussed in detail elsewhere; however, some of their benefits include decreased platelet aggregation, blood viscosity, and fibrinogen; antioxidant properties; and lower incidences of chronic disease, including cardiovascular disease and certain cancers, in particular, prostate, breast, and lung cancer (Zetzl and Marangoni, 2012). Clearly, the addition of any one of these compounds to an oleogel would have a significant impact on its healthiness. The

availability/presence of dietary fat also has a significant impact on the absorption of most of the aforementioned molecules, as they are all at least partly fat soluble.

The difficulty in incorporating any one of these nutraceutical compounds lies in trying to minimize their degradation. Many of these compounds contain a large number of double bonds , and they would degrade very quickly if exposed to the high heat required to create an ethylcellulose oleogel, for example. By adding these compounds during the cooling process, just before gelation occurs, this could maximize the quality and effectiveness of any added nutraceuticals.

Phytosterol–Oryzanol Mixtures for Oraganogelation Purposes

Phytosterols are compounds of particular interest, as they not only possess cholesterol-reducing properties, but also certain varieties can be used as organogelators (Bot and Flöter, 2011). Mixtures of β-sitosterol and γ-oryzanol in vegetable oil can be used to form optically transparent (when a 1:1 molar ratio of structurant is used) or hazy/semi-opaque gels at incorporation levels as low as 2–4% total sterols at 5 °C (Bot and Flöter, 2011; Bot et al., 2009). It is proposed that these components are able to structure the vegetable oil by forming tubules with a diameter of approximately 7.2 nm and a wall thickness of 0.8 nm (Bot and Flöter, 2011). These tubules are able to aggregate and interact, effectively forming a network and entrapping the liquid oil (Co and Marangoni, 2012). The small size of these tubules—smaller than the wavelength of visible light—gives an explanation as to why they are able to form optically transparent gels (Bot and Flöter, 2011). Although these phytosterol–oryzanol mixtures are very effective at gelling oil when used together, this gelation does not take place when one of the components is excluded. Instead, sterol or sterol ester crystals are formed and simply settle to the bottom of the container without gelling or structuring the liquid oil (Co and Marangoni, 2012).

The β-sitosterol and γ-oryzanol mixture in vegetable oil is one of the first oleogel systems that consists entirely of food-grade or near-food-grade materials (Bot and Flöter, 2011). This is a major step forward in the field of organogelation, as most organogelators to date have not been even given GRAS (generally recognized as safe) status or letters of no objection from governing bodies (Co and Marangoni, 2012). An extensive summary of the β-sitosterol and γ-oryzanol system was completed by Bot and Flöter (2011), providing a concise review of the work completed on these components as organogelators thus far.

Although the prospect of phytosterol-based oleogels appears very promising, they unfortunately suffer from significant limitation in regards to food applications. In the presence of water, the surfactant-like organogelatorshave a reduced ability to structure

oil (Bot and Flöter, 2011). In a system such as a baked good or meat emulsion, compatibility with water is a critical property. Because the gelling capabilities of β-sitosterol and γ-oryzanol are so greatly affected by water, it has been suggested that they will most likely only be effective gelators in an anhydrous system (Bot and Flöter, 2011). Moreover, most low-molecular weight gelators that form self-assembled fibrillar networks are extremely shear sensitive. This is unfortunate since most food manufacturing processes as well as the actual food consumption involve high levels of shear. In addition, the high cost of sterols and sterolesters further renders these organogelators applicable for only more specific applications, where a greater cost can be justified. Therefore, even with the promising health benefits of such a nutraceutical organogelator, it is unlikely that we will be seeing a phytosterol-based oleogel on supermarket shelves in the near future.

Even though clearly many technical challenges still exist, there have been great advancements in recent replacements for TFAs, in particular, the development of structured emulsions using monoglycerides and edible oleogels. The promise of incorporating additional nutraceuticals into these substitutes further increases their value, as they would become essentially free of unhealthy fatty acids and would contain highly beneficial nutraceuticals. Due to these factors, both structured emulsions and certain edible oleogels could be considered "solutions" to the *trans* fat problem.

Conclusion

Although many promising solutions to TFAs have been proposed and are currently in use, development is still required to ensure that we are not just simply substituting *trans* fats with something that is equally, or similarly, harmful. We should attempt to develop solutions that not only provide all the requirements of a viable substitute, but also ideally contain components or ingredients that actually improve our cardiovascular health, such as phytosterols or polyunsaturated fatty acids. With the development of many functional and comparatively healthy replacements over the past five years, such as oleogels and structured emulsions using monoglycerides, it is possible that we may be able to overcome the *trans* fat problem in the near future.

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