The development and characterisation of a structured oil system: Ethylcellulose oleogels and water-in-oil oleogel-emulsions

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Abstract

This study investigated the gel behaviour displayed by ethylcellulose oleogels and oleogel emulsions. Oleogel behaviour focused on gels made with 7-10 w/w% ethylcellulose and either canola oil, sunflower oil or soyabean oil. There was no significant difference in rheological properties as all gels demonstrated viscoelastic shear thinning behaviour. The gels demonstrated some ability to recover viscosity after shear as demonstrated by a 3 interval thixotropy test. Oleogel emulsions were made with 3-5 w/w% ethylcellulose and 20-50 w/w% water. The 3 w/w% gels were able to stabilise 50 w/w% water, whereas the 5 w/w% gel was able to stabilise 20 w/w% water. Retrogradation was observed when a gel solution of 5 w/w% ethylcellulose and 50 w/w% water was emulsified, like that observed in starch gels.

Oleogel emulsion stability was observed through microscopy and proved to be relatively stable for 28 days. Limited oil separation was observed at the top of the sample during storage, but no water separation was visible. The samples were more stable when stored at chilled temperatures, and emulsion stability at elevated temperature was better than expected. The application of oleogels into W/O based food such as ice cream, margarine, cream cheese, or spreads is a popular research area due to the potential for replacing coconut, palm, and animal-based fats. This report has demonstrated that ethylcellulose can create stable, gelled, W/O oleogel emulsions which is promising for reducing saturated fat in food applications.

Acknowledgements

An interest in oleogels was sparked during my time working for Bakels Edible Oils (NZ) Ltd. Leaving a commercial role to pursue this research was a very challenging experience in many ways, but the personal and analytical skills gained throughout this degree will be invaluable throughout the rest of my career. I am deeply grateful for the support of my supervisor, Professor Matt Golding, for his positive and calm attitude towards this project. I am also very thankful for the support and guidance from Steve Glasgow, Michelle Tamehana, and Professor Richard Love.

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List of Abbreviations

AP	Aqueous phase
CAN	Canola
CO	Canola oil
CW	Candellia wax
DSC	Differential scanning calorimetry
EC	Ethylcellulose
FA	Fatty acid
FAP	Fatty acid profile
FDA	U.S. Food and Drug Administration
FP	Fine particle
FSANZ	Food standards Australia and New Zealand
GMO	Glycerol monooleate
GMP	Good manufacturing practice
GMS	Glycerol monostearate
GRAS	Generally regarded as safe
HMOG	High molecular weight oleogelator
LDL	Low density lipoprotein
LMOG	Low molecular weight oleogelator
LVR	Linear viscoelastic region
ND	Not detected
O/W	Oil in water

PGPR	Polyglycerol polyricinoleate
PUFA	Polyunsaturated fatty acid
RBX	Rice bran wax
REA	Ricinelaidic acid
SA	Stearic acid
SAXS	Small angle x-ray scattering
SBO	Soyabean oil
SFO	Sunflower oil
SMO	Sorbitan monooleate
SMS	Sorbitan monostearate
SO	Stearyl alcohol
TAG	Triacylglycerol
TMS	Triglyceride monostearate
TPA	Texture profile analyser
USAXS	Ultra small angle x-ray scattering
WAXS	Wide angle x-ray scattering
W/O	Water in oil
12-HSA	12-Hydroxystearic acid

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1.0 Introduction

Edible fats and oils provide essential nutrients (López-Pedrouso et al., 2021) and influence food properties such as flavour, texture, shelf-life, mouthfeel, and spreadability (Hwang, 2020). The structure consists of triglycerides (TAGs), which is three fatty acids (FA) esterified onto a glycerol backbone (Davidovich-Pinhas et al., 2016; López-Pedrouso et al., 2021). The FA composition determines whether the resulting phase is a liquid or solid due to the degree of TAG crystallisation. FAs fall into the following major groups; saturated, *cis* or *trans* monounsaturated, or *cis* polyunsaturated. Fats with more saturated FAs correspond to a more solid structure as saturated FAs have a higher melting point meaning the TAG crystals can maintain a solid structure at room temperature (López-Pedrouso et al., 2021). Saturated fats and *trans* fats in particular are known to increase low-density lipoprotein (LDL) cholesterol which is linked to cardiovascular health issues such as heart disease (Food Standards Australia New Zealand, 2017; Patel & Dewettinck, 2016), metabolic syndrome (Hwang, 2020), type 2 diabetes, high blood lipid content, inflammation, oxidative stress, endothelial dysfunction, and high body weight (López-Pedrouso et al., 2021).

Trans fats are naturally present in fats of animal origin due to bacterial fermentation (Lichtenstein, 2016), however, the primary source of *trans* fats in consumer diets used to be from partially hydrogenated vegetable oil (Food Standards Australia New Zealand, 2017). Partial hydrogenation is a manufacturing process that was used to change the state of vegetable oil from liquid-like to solid-like, mimicking the solid structure of animal-sourced fats such as tallow and milk fat. However, this process changes the chemical structure of vegetable oils, specifically orientation of monounsaturated bonds from cis to *trans*. Once the US Food and Drug Administration (FDA) realised the carcinogenic nature of trans fat, the generally regarded as safe (GRAS) status was removed in 2015 and a total ban on partially hydrogenated oil was put in place from 2020 (Hwang, 2020). FSANZ (2017) now recommends that saturated fats consumption is limited to 10 w/w% or less of a persons' calorific intake. *Trans* fat intake should be avoided wherever possible, and both saturated and *trans* fats should be replaced with mono and polyunsaturated fats (Food Standards Australia New Zealand, 2017; López-Pedrouso et al., 2021). The solid-like texture of partially hydrogenated oils plays a significant role in creating the

texture and mouthfeel of foods and finding a suitable replacement is not a simple task for food manufacturers. Coconut, palm, and fully hydrogenated oils are popular replacements; however, these alternatives all have high levels of saturated fats (Hwang, 2020). This shift has created demand for structured oils based on polyunsaturated fatty acids (PUFAs) which can mimic the appearance, palatability, and textural characteristics of saturated and *trans* fats.

Research into structured oils began with organogels which were designed for the replacement of petroleum in cosmetic (Davidovich-Pinhas et al., 2015) or industrial products (Sánchez et al., 2011). One of the first mentions of an oleogel was by (Aiache et al., 1992) who used ethylcellulose (EC) to alter the consistency of vegetable oil. A comment was made that "many applications can be foreseen in pharmaceutical and cosmetic applications where the use of natural vegetable oils as vehicles for drugs is large" (Aiache et al., 1992). Further developments were then made by Gandolfo et al. (2004) who trialed different formulations of FAs and fatty alcohols when looking into the texture of structured vegetable oils. The connection was then made between structuring oils and saturated fat replacement. Laredo et al. (2011) built on work by Aiache et al. (1992) to further understand the rheological properties of EC oleogels, and acknowledged the potential for application in several different fields, including food applications.

Recent research in this area splits into two areas, formulating oleogels for specific food application such as meat products (Alejandre et al., 2019; He et al., 2021; López-Pedrouso et al., 2021; Moghtadaei et al., 2021), chocolates (Li et al., 2021), and shortenings for baked goods (Ye et al., 2019). The second area of research is on oleogels with an encapsulated phase or active ingredient (Gao et al., 2021; García-González et al., 2021; Lefroy et al., 2021; Wijarnprecha et al., 2019; Wijarnprecha et al., 2019; Wijarnprecha et al., 2021). This report aims to summarise existing research on oleogel structure, function, and characterization for the purpose of identifying key areas which look promising for further development into commercial products.

2.0 Literature Review

2.1 Oleogelators

Oleogelators, or gelators, are the structuring agents added to liquid oil which can self-assemble into a three-dimensional structure and increase the viscosity of the liquid oil imparting viscoelastic properties to the resulting solution. Gelators are commonly categorized into two groups based on molecular weight, low molecular weight oleogelators (LMOGs) and high molecular weight oleogelators (HMOGs). LMOGs self-assemble into a crystal network to bind oil, examples include FAs, fatty alcohols, waxes, phytosterols, and mono- and diglycerides (Co & Marangoni, 2018; Hwang, 2020; Singh et al., 2017). HMOGs use physical or chemical interactions to form a supramolecular network of polymers, examples include EC, proteins, and polysaccharides (Ashkar et al., 2019; Co & Marangoni, 2018).

Oleogel structuring has been described as the ordering of "building blocks" (supramolecular assembly of particles) and there are four common methods including (1) crystalline particles, (2) self-assembled structures of LMOGs (liquid crystal structures: fibers, strands, tubules, mesophases, inverse micelles), (3) self-assembled structures of polymers, or polymeric strands, (4) miscellaneous structures (Patel, 2018).

Described as one of the most promising gelators, EC is the only currently known polymer to be soluble in oil (Gravelle & Marangoni, 2018a). EC has FDA approval for use in foods due to its status as a non-digestible food grade biopolymer (Ahmadi et al., 2020). It is used to improve formulations such as cream-based cosmetic products, industrial products such as printing inks, ceramides, lacquers, pharmaceutical products as a diffusion barrier, or tablet binder for controlled release coatings (Gravelle & Marangoni, 2018a). Exposure to an alkaline environment and subsequent exposure to chloroethylene gas chemically alters cellulose by partially replacing hydroxyl end groups with ethyl end groups to form EC (Davidovich-Pinhas et al., 2015; Gravelle et al., 2012). This results in an ethoxy content of between 48-49.5% which allows the characteristic oil solubility (Ahmadi et al., 2020; Davidovich-Pinhas et al., 2016; Fu et al., 2020; Gravelle & Marangoni, 2018a).

Table 1 List of common oleogelators and the type of structure they use to self-assemble into a 3D matrix

Type	Gelator	Structure	Reference
Plant waxes	Candelilla wax, Rice bran wax, Carnauba wax, Sunflower wax	Waxes are long chain esters derived from fatty acids and fatty alcohols, also contain minor components such as n-alkanes, alcohols, and sterol esters, esters of pentacyclic triterpenoids.	(Blake et al., 2018)
Animal waxes	Beeswax, Shellac wax	Beeswax is predominantly based on straight-chain mono-hydric alcohol compounds and hydroxyl esters. Purified resin from the secretion of lac insects, shellac consists of polyhydroxy polycarboxylic esters, alcohols, acids, and alkanes	(Patel, 2018)
Plant sterols and sterol esters	β-sitosterol γ-oryzanol	The components of this plant sterol and sterol ester form unique tubules which aggregate to form a firm network.	(Bot & Flöter, 2018)
Sphingolipid	Ceramide	Like phytosterols, ceramides exhibit nutraceutical properties but are very costly. They crystallise into a fibrillar or needle-like crystals in vegetable oil.	(Rogers, 2018b)
Polymers	EC Whey protein Chitin	Polymeric strands form thin fibrous networks	(Scholten, 2018; Singh et al., 2017)

Lipids	Mono and diglycerides	Glycerol molecule esterified onto one or two fatty acids, can self-assemble into an inverse lamellar crystal structure.	(Ashkar et al., 2019; Chen & Terentjev, 2018)
Fatty acid	Oleic acid, 12-hydroxystearic acid (12-HSA) Ricinelaidic acid (REA)	Long chain fatty acids are capable of gelling oil at low concentrations, the gels are stabilised by long, thin, fibrous structures.	(Rogers, 2018a)
Fatty alcohol	Stearyl alcohol	Crystalline TAGs self-assemble into a solid network	(Valoppi et al., 2018)

While a variety of different structuring agents have proved successful, the criteria for creating a commercial food product means that many structuring agents are not currently feasible for the food industry. Structuring agents must be approved as an FDA food ingredient, have GRAS status as a food additive, as well as being commercially available and economically viable (Blake et al., 2018). While some gelators may have GRAS status, they also need to be approved for use in the intended food application, for example, meat products, margarines, ice cream or spreads (López-Pedrouso et al., 2021). The cost of ingredients also need to be taken into consideration, structuring agents such as phytosterols and ceramides have proven to be very effective and provide nutraceutical benefits, however, the current market price means they are not economically viable for use in food applications (Co & Marangoni, 2018).

2.1.1 Surfactants

All gelators have strengths and weaknesses, therefore research has been dedicated to investigating how gel structure can be further improved in terms of gel strength, plasticity and thermal response by adding surfactants (Gravelle et al., 2014). Research has been focused on the synergistic effect of a gelator-gelator or gelator-surfactant combination. In successful cases, the concentration of gelator required to achieve a solid-like gel is reduced, making the formulation more cost effective and more-likely to align with food regulatory requirements. Two examples of this are the plant sterol and sterol ester combination, γ-oryzanol and β-sitosterol, as well as the fatty alcohol and FA combination, stearyl alcohol and stearic acid (SO:SA). This report will continue with a focus on oleogels structured by EC, therefore please refer to the reference articles in table 1 to find further reading material on alternative gelators and structuring methods.

Surfactants consist of non-polar tails and polar head groups which carry a positive or negative charge. The charges can create surfactant-polymer interactions and influence the gel structure. Increased gel strength has been observed in some gels with surfactant addition (Davidovich-Pinhas, Barbut, et al., 2015), which suggest that the surfactant-polymer interactions are supporting the crystallised oleogel three-dimensional network. The potential for surfactants to improve gel properties is dependent on its compatibility with EC. The surfactant must work as a plasticizer and interact with the polymer backbone through hydrogen bonding or Van der Waals forces (Davidovich-Pinhas et al., 2015).

While surfactants have demonstrated their ability to support solvent-solvent and polymer-solvent interactions, there is more to be understood regarding how the surfactant molecules interact with the gelator network, and the mechanism in which they work to improve gel strength. Research by Davidovich-Pinhas et al. (2015) found that glycerol monooleate (GMO) and glycerol monostearate (GMS) was successful in lowering the gel point temperature for EC to dissolve in oil which is useful for saving energy, time, and minimizing the effects of oxidation on the oil phase. Davidovich-Pinhas also identified that the surfactant molecules have a ‘stiffening’ effect on the polymer backbone, therefore increasing gel hardness. Fasolin et al.

(2018) suggested that there appears to be more interaction between glycerol based surfactants compared with sorbitan based surfactants in supporting the structure of EC oleogels.

Table 2 List of common oleogel surfactants and the observed effect on an EC oleogel

Gelator	Solution	Observations	Reference
Soy lecithin	10 w/w% 20cP EC 1 w/w% Lecithin	Addition of soy lecithin to an EC oleogel formulation increased mechanical strength of resulting gel. Rheological properties comparable to lard.	(Aguilar-Zárate et al., 2019; Hwang, 2020)
Stearyl alcohol and stearic acid (SO:SA)	7:3 ratio of EC:SOSA	The use of SO:SA with EC demonstrates an improvement gels strength, plasticity, and gel flow behaviour.	(Gravelle & Marangoni, 2018b)
Glycerol Monooleate (GMO)	11 w/w% EC 3.67 w/w% GMO	Decrease in sol-gel and gel-sol transition temperature was observed. Notes: GMO was more effective than SMO.	(M Davidovich-Pinhas, S Barbut, et al., 2015)
Glycerol monostearate (GMS)	11 w/w% EC 3.67 w/w% GMS	GMS appears to interact with the polar areas of the EC structure. A significant increase in gel strength was observed when EC and GMS were used together.	(M Davidovich-Pinhas, S Barbut, et al., 2015)
Sorbitan monooleate (SMO)	11 w/w% EC 3.67 w/w% SMO	Decrease in sol-gel and gel-sol transition temperature was observed.	(M Davidovich-Pinhas, S Barbut, et al., 2015)
Sobitan Monostearate (SMS)	3.3% w/w SMS 10% w/w 45cP EC	Decreases in average pore size were observed, smaller pore sizes are correlated with increased gel strength.	(Zetzl et al., 2014)

		An increase in gel elasticity was also recorded.	
Triglyceride monostearate (TMS)	1% w/w TMS 4% 100cP EC	Microstructure was comparable to that of Crisco shortening, had good air-incorporation ability when used in a shortening and baked bread.	(Ye et al., 2019)

2.2 Oil

Functional properties of fats and oils can be manipulated through altering the fatty acid composition or processing conditions (Gravelle et al., 2016). Manipulation through processing conditions can include hydrogenation (partial or full) and fractionation. Altering the fatty acid profile is very common as this is easily done by blending different oils together to achieve a desired melting profile.

As different oils can impart different rheological, textural, and thermal properties onto a food application it is unsurprising that oil type is reported to also influence the properties of oleogels (Pehlivanoglu et al., 2018). A full understanding how the FAP of the solvent phase affects the three-dimensional structure formed by the gelator would allow researchers to optimize oil blends for a specific gelator and application.

As discussed, saturated FAs contain high melting TAGs, which allows them to maintain a solid texture at higher temperatures than liquid oils (Gravelle et al., 2016). Coconut oil, palm oil, and their derivatives are commonly used as a base fat in food products due to being inexpensive, easily accessible and having a melting point above room temperature. These properties result from the high amount of lauric acid (C12:0) in coconut oil, and palmitic acid (C16:0) in palm oil. A comparison of the FAPs of coconut oil, palm oil, canola oil, soyabean oil, and sunflower oil is demonstrated in table 3.

Table 3 A comparison of the fatty acid profiles of common plant-based oils

`	Coconut Oil	Palm Oil	Rapeseed Oil	Soyabean Oil	Sunflower-seed Oil
C6:0	ND-0.7	ND	ND	ND	ND
C8:0	4.6-10.0	ND	ND	ND	ND
C10:0	5.0-8.0	ND	ND	ND	ND
C12:0	45.1-53.2	ND-0.5	ND	ND-0.1	ND-0.1
C14:0	16.8-21.0	0.5-2.0	ND-0.2	ND-0.2	ND-0.2
C16:0	7.5-10.2	39.3-47.5	1.5-6.0	8.0-13.5	5.0-7.6
C16:1	ND	ND-0.6	ND-3.0	ND-0.2	ND-0.3
C17:0	ND	ND-0.2	ND-0.1	ND-0.1	ND-0.2
C17:1	ND	ND	ND-0.1	ND-0.1	ND-0.1
C18:0	2.0-4.0	3.5-6.0	0.5-3.1	2.0-5.4	2.7-6.5
C18:1	5.0-10.0	36.0-44.0	8.0-60.0	17.0-30.0	14.0-39.4
C18:2	1.0-2.5	9.0-12.0	11.0-23.0	48.0-59.0	48.3-74.0
C18:3	ND-0.2	ND-0.5	5.0-13.0	4.5-11.0	ND-0.3
C20:0	ND-0.2	ND-1.0	ND-3.0	0.1-0.6	0.1-0.5
C20:1	ND-0.2	ND-0.4	3.0-15.0	ND-0.5	ND-0.3
C20:2	ND	ND	ND-1.0	ND-0.1	ND
C22:0	ND	ND-0.2	ND-2.0	ND-0.7	0.3-1.5
C22:1	ND	ND	>2.0-60.0	ND-0.3	ND-0.3
C22:2	ND	ND	ND-2.0	ND	ND-0.3
C24:0	ND	ND	ND-2.0	ND-0.3	ND-0.5
C24:1	ND	ND	ND-3.0	ND	ND

Not detected (ND) defined as < 0.05% Data sourced from Codex Alimentarius (1999)

Structuring the FAP of an oil blend can be nutritionally beneficial. Gómez-Estaca et al. (2019) successfully improved the FAP of pork burgers through the use of oleogels made with olive oil, linseed oil, and fish oil. However, it was recommended that further development was needed to delay oil oxidation and improve the sensory properties.

Martins et al. (2018) reported that the unsaturated FA composition of the oil is the most important factor influencing gel properties. Scharfe and Flöter (2020) agreed with these findings and explained that a higher degree of unsaturated corresponds to increased gel hardness. This is thought to occur as unsaturated FAs have more conformational flexibility which allows for a more tightly packed structure (Laredo et al., 2011). Greater levels of unsaturation also allow for a greater number of interpolymer junction zones, allowing for more

interpolymer bonds to form, thereby increasing gel strength (Davidovich-Pinhas et al., 2016; Gravelle et al., 2016; Scharfe & Flöter, 2020). Other factors known to increase gel hardness include longer chain length, increased hydrophobicity, and higher molar volume (Laredo et al., 2011; Martins et al., 2018; Scharfe & Flöter, 2020).

2.2.1 Solvent polarity

Gel hardness has been proven to increase with increasing solvent polarity (Aguilar-Zárate et al., 2019). As the number of polar compounds increases so does the number of hydrogen bonds between polymer strands. If the solvent is apolar, such as mineral oil, then no bonds can form and EC will precipitate out of solution (Gravelle et al., 2012). The number of polar compounds can be increased by adding a highly polar oil, such as castor oil, to the solvent phase. Giacintucci et al. (2018) found that olive oil oleogels were stronger when made with extra virgin olive oil compared to refined olive oil, as the refining process removes polar minor compounds, thus decreasing the polarity of the oil.

Another factor affecting solvent polarity is oxidation. Polar compounds form as a by-product of oxidation which can allow new hydrogen bonds to form between polymer strands and increase gel strength (Gravelle et al., 2012). The more hydrogen bonds formed, the greater increase in gel strength. Oxidation will be discussed further in the next section.

2.3 Ethylcellulose oleogels

EC is a popular structuring agent as it can be directly dispersed in oil. Other polymers of a similar nature require indirect dispersion which involves extra steps so the gelator can be dispersed in the continuous phase. On a microscopic level, EC dispersed in oil forms a coral-like 3D network of strands and bundles which is stabilised by intra- and interpolymer bonds, hydrogen bonds (Martins et al., 2018), and van der Waals interactions (Gravelle et al., 2012). The coral-like structure is created by the pores of immobilised oil encapsulated in the EC matrix (Gravelle et al., 2018).

EC exhibits viscoelastic properties when dispersed in oil and heated above the glass transition temperature (Gravelle et al., 2018). It is also available in different viscosity grades. The length of the EC carbon chain determines how the polymers are structured, this has been shown through X-ray scattering (Martins et al., 2018). A longer carbon chain results in a higher molecular weight and increased viscosity (Gravelle & Marangoni, 2018a). The critical concentration of EC for the structure to form a set gel is dependent on the EC viscosity and the FAP of the oil (Gravelle et al., 2012).

Direct dispersion of EC in oil requires the solution to be heated above the glass transition temperature (T_{glass}) which ranges from 125-140°C depending on polymer molecular weight (Gravelle et al., 2018). Upon reaching T_{glass} , the polymer changes from a solid to a rubbery state (Ahmadi et al., 2020). Once the temperature is decreased and the solution is cooled below gel point temperature (T_{gel}) the solution sets into a thermo-reversible viscoelastic gel. T_{gel} varies depending on polymer concentration and molecular weight (Davidovich-Pinhas et al., 2015).

Molar volume also influences the gel system. Laredo et al. (2011) explain that a larger molar volume allows EC strands to spread further apart which helps with solubility but can decrease the number of hydrogen bonding sites, reducing gel strength.

2.3.1 Characterisation

Characterising oleogels allows researchers and industry professionals to gain more in-depth understanding of variables involved with oleogel development and optimisiation. Characterising gives insight into the gelation mechanism, and how to increase gel hardness, elasticity, and shelf life. It enables researchers to compare between samples and different formulations to prove which will provide the desired properties.

2.3.1.1 Glass transition temperature (T_{glass})

As discussed, T_{glass} signifies a phase change from a solid powder to a rubbery, viscous liquid (Ahmadi et al., 2020). EC melts between 165-173°C bu_t heat increases the rate of oil oxidation and EC is known to degrade and act as a pro-oxidant between 180-200°C. Therefore, it is not advised to heat oleogels any higher than necessary. Differential scanning calorimetry (DSC) has been used by researchers to observe the dissolution, gelation and any further thermal events occurring when EC and oil are heated and cooled in a system. An analysis by Davidovich-Pinhas et al. (2015) is displayed in figure 1.

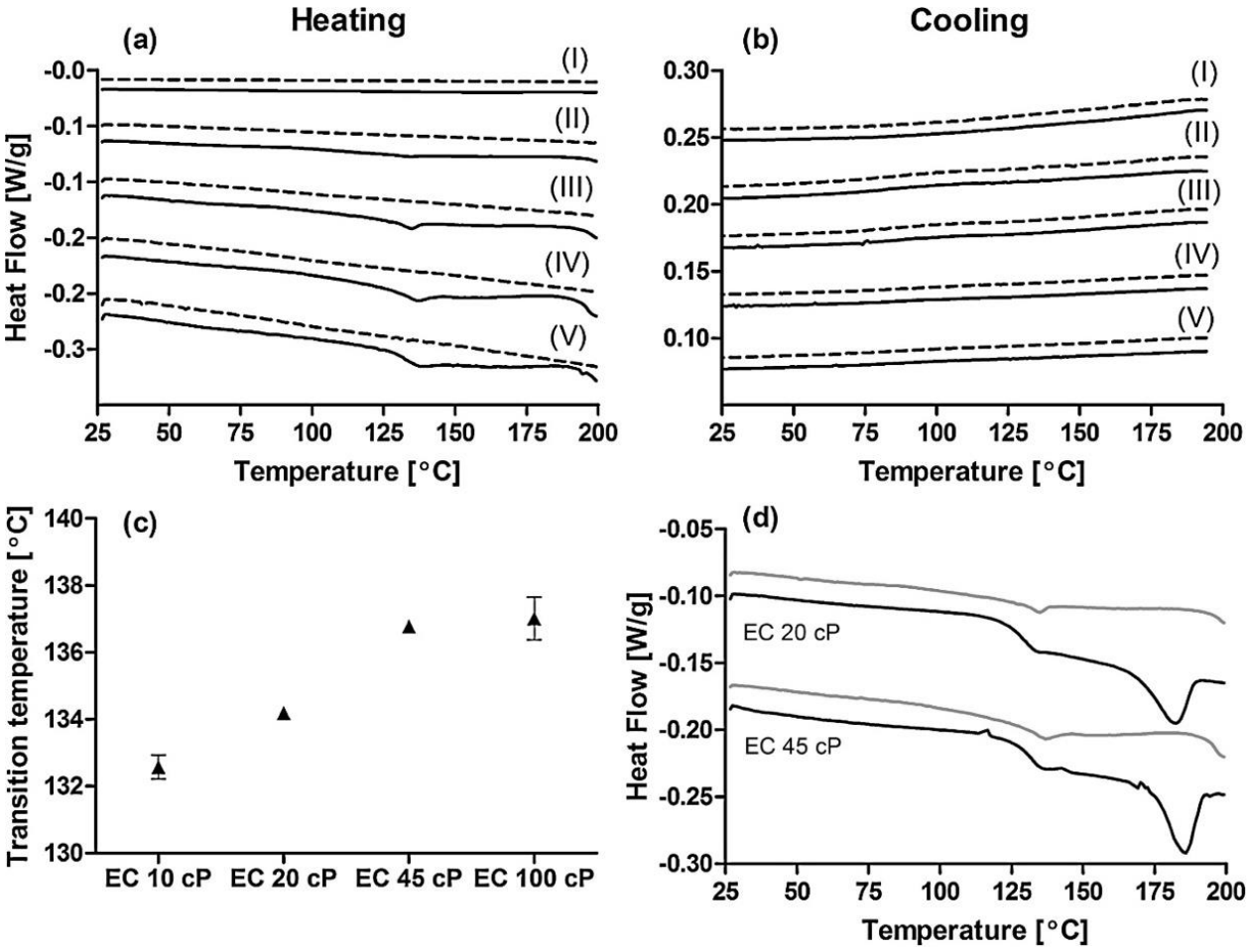


Figure 1 DSC thermogram during two cycles of heating (a) and cooling (b) canola oil (I) with EC 10 cP (II) 20cP (III) 45cP (IV) and 100 cP (V) at a rate of 5°/minute. The solid line represents the first cycle, and the dashed line represents the second cycle. Peak transition temperatures during heating are shown in (c). A comparison of the thermograms obtained during heating EC

powder (black) and an EC and canola oil solution (grey) is shown in (d). Reprinted with permission from Elsevier Inc.

2.3.1.2 Gelation

Gelling is initiated when the temperature of the solution drops below T_{glass}. Although T_{glass} can vary with molecular weight, the general temperature range is 100 – 130°C. This creates thermo-reversible physical gels, similar to other polysaccharide gel systems such as agarose, carrageenan and gellan gum (Davidovich-Pinhas et al., 2015). The exact point of gelation is referred to as gel point temperature or T_{gel}. This can be difficult to pinpoint visually so rheological tests, such as a temperature sweep test, can been performed to identify the transition. This can be identified as when the loss modulus (G') and storage modulus (G") crossover signifying a sol-gel transition (Davidovich-Pinhas et al., 2015). G' and G" are parameters used in rheology to describe the state of the solution at a point in time. When G'' > G' behaviour is observed, this indicates the sample has liquid-like behavior. Whereas when G' > G'' is observed, this indicates solid-like gel behaviour (Ashkar et al., 2019). These parameters are frequently used in rheology to describe gel behaviour as a function of variables such as time, temperature, strain, and frequency.

Hydrogen bonding is responsible for the rigidity of the solid gel created by EC oleogelation. This occurs through inter and intramolecular interactions as the polymer chains self-assemble into a scaffold-like structure. This was proved during early research into oleogels by Laredo et al. (2011).

2.3.1.3 Cooling Rate

The cooling rate of the solution has a significant impact on the strength of the resulting gel, faster cooing rates have been shown to have a reduced gel strength (Martins et al., 2018). Davidovich-Pinhas et al. (2015) explains that during cooling EC is changing phase which involves molecular rearrangement of polymer chains into a three dimensional structure. The longer that the solution has to cool, the more organized and stable the resulting structure will be. However, the importance of cooling rate is dependent on the molecular weight of the gelator. LMOGs form harder gels when allowed to cool at a slower rate but there does not appear to be a

significant difference for HMOGs which have longer carbon chains. Davidovich-Pinhas et al. (2019) observed that 10cP and 20cP EC was more affected by cooling rate compared with 100cP EC due to the higher molecular weight. The cooling rate reduces the gel storage modulus at gel state. Lastly, EC gels require static cooling due to the physical nature of the junction zones (Gravelle et al., 2018) as agitation will disrupt the formation of the 3D matrix.

2.3.1.4 Gelation kinetics

Looking into the microstructure of oleogels allows researchers to see the impact of different variables on a molecular level. Oleogels form a porous structure upon cooling which is caused by a coral-like network of EC strands or bundles encapsulating the liquid oil (Fu et al., 2020). Two of the key factors influencing pore size is the level of unsaturated oil and the concentration of EC in the system (Zetzl et al., 2014). A greater level of unsaturated oil corresponds to a smaller pore diameter and increased polymer concentration can also decrease pore diameter, resulting in increased gel hardness.

Polarised light microscopy is used for characterizing the microstructure of the crystallised gelator. Researchers such as Godoi et al. (2019) have been able to capture images of the crystalline networks formed by different gelators. X-ray scattering techniques have also enabled researchers to detect structural attributes. Small angle or wide angle x-ray scattering (SAXS/WAXS) can provide information about the molecular arrangement and packing, whereas ultra-small x-ray scattering (USAXS) can show the self-assembly and aggregation of particles (Gravelle et al., 2018).

2.2.1.5 Materials testing

The most popular textural property of oleogels is gel hardness. A texture profile analyser (TPA) looks at a range of attributes including hardness, cohesiveness, springiness, fracturability, chewiness, gumminess and resilience but the two most relevant properties for this application are hardness and cohesiveness as these provide an indication of the gel's ability to withstand sequential deformations that are experienced during mastication (Ashkar et al., 2019). While increased hardness can be beneficial for an oleogel, it is not necessarily an ideal property in a food application as hardness can be a sign of staling (Adili et al., 2020). Hardness is a popular

attribute due to the likeness between oleogels and common fats such as palm oil and tallow. However, hardness in a final application is generally not an ideal attribute, especially with bakery products like cakes, muffins, and breads.

An example by Davidovich-Pinhas et al. (2015) of how a TPA has been used for oleogel research is shown in figure 2. In this example, a compression test was used to test the effect of gelation setting temperature on oleogel mechanical properties (fracture point and hardness). This demonstrated a positive correlation between gel setting temperature and gel hardness.

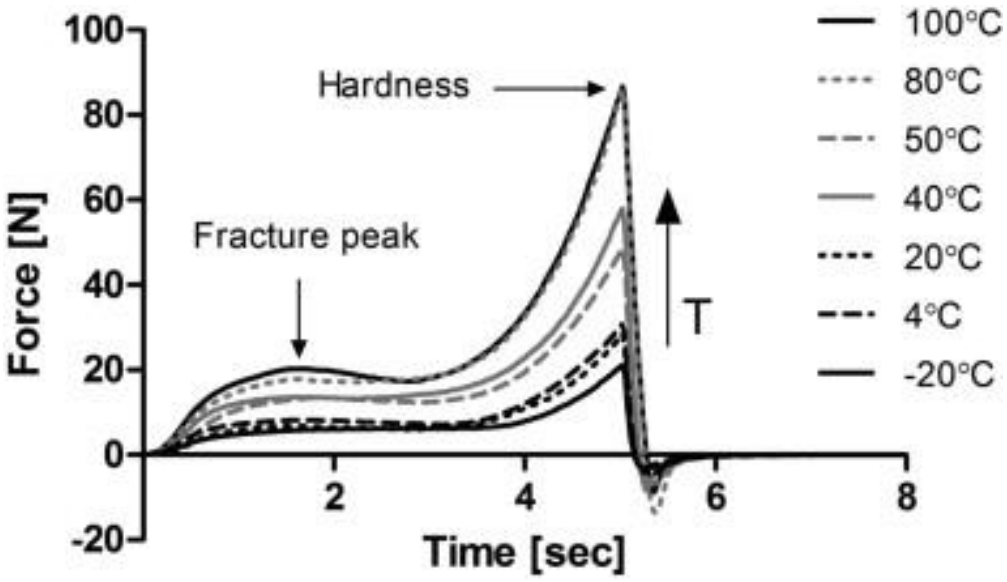


Figure 2 Characteristic single compression cycle curves for 15 w/w% EC 20cP in canola oil at different gelation temperatures. Arrow indicates increasing gelation temperature. Reproduced with permission from Elsevier Inc.

The type of oil used influences the textural properties of an oleogel. Zetzl et al. (2014) looks into a series of gels formed using 10% w/w EC and either canola, soyabean, or flaxseed oil. The TPA was able to measure the hardness of the different gels formed and confirmed that there was a significant difference in hardness between these gels, thus confirming the correlation between gel strength and type of oil.

2.3.2 Oxidative stability

Unsaturated FAs are less stable than saturated FAs as they have at least one double bond, increasing the risk of oxidation. With oleogels, one of the objectives is to replace saturated FAs with unsaturated FAs, therefore, increased oxidation is a consequence that requires attention. Overall, the oxidative stability of oleogels is not yet fully understood (Fu et al., 2020). The rate of oxidation on the immobilised oil within the gel matrix is difficult to test and the development of new testing methods may be required as standard oil oxidation test methods may not be appropriate for a gelled oil.

EC has been found to act as a pro-oxidant when used in high concentrations (Fu et al., 2020) or is heated to temperatures above 180°C (Kim et al., 2014). As the EC and oil solution needs to be heated above 125°C (Gravelle & Marangoni, 2018a) for EC to be soluble, this increases the rate of oxidation (Martins et al., 2018). Gravelle et al. (2012) pointed out that the effect of high temperatures on the functionality of EC is unknown, high temperatures can cause polymers to breakdown which could reduce gel strength. Oxidation negatively affects the sensory properties of oil, but the effect that oxidation and the degradation of EC will have on an oleogel and any subsequent food applications is also unknown.

Kim et al. (2014) found that the oxidative stability of EC oleogels is dependent on temperature, time, and concentration. Oil stability is also an important factor, and it is unknown if there are any effects caused by the interactions between the oil and EC that may inhibit or increase oxidation. Synthetic and natural antioxidants are commonly used in oil to delay oxidation, however, another area requiring research is if the antioxidants will aid in delaying EC oxidation, and how the inclusion of antioxidants will affect the overall gel system.

For now, it is known that the longer the solution is exposed to heat, the faster oxidation will occur. To control and monitor this, Fu et al. (2020) recommends heating oil to the T_{glass} efficiently with minimal holding time at T_{glass} to ensure dissolution while minimizing oxidation.

2.4 Potential applications

Oleogels could be incorporated into any food application that has a solid oil or fat phase. However applications should not be limited to the food industry, oleogels have already been incorporated into industrial and cosmetic products and there is potential for pharmaceutical and nutraceutical applications too.

Other properties of oleogels that have been identified include emulsion stabilization, controlled rate of nutraceutical release, reduced oil migration, fat mimetic (Gravelle et al., 2012), heat resistance, oil binding agent, and textural ingredient in cosmetic products (Davidovich-Pinhas et al., 2015).

Table 4 outlines different applications for oleogels with a primary focus on food applications however some other applications have also been included.

Application	Oleogelator	Gelator (%)	Oil Phase	Reference
Beef Burger	EC 10cP	10	Sesame	(Moghtadaei et al., 2021)
Pork burgers	EC Beeswax	Not mentioned	Olive, linseed, fish oils	(Gómez-Estaca et al., 2019)
Frankfurter	EC	8-10	Canola oil	(López-Pedrouso et al., 2021)
Frankfurter	Monoglycerides Phytosterols	15 5	sunflower oil	(Kouzounis et al., 2017)
Breakfast sausage	EC	8-14	Canola oil	(López-Pedrouso et al., 2021)
Shortening	Carnauba wax	5	Palm/ cottonseed/ palm kernel/ palm stearin	(Pehlivanoglu et al., 2018)

Shortening	EC 100 cP	4	Palm Stearin/Soyabean (30% saturation)	(Ye et al., 2019)
Margarine	Candelilla wax	2.7	High oleic sunflower oil	(da Silva et al., 2018)
Cream cheese	EC	0.76*	High oleic soyabean	(Bemer et al., 2016)
Chocolate spread	Monoglyceride Beeswax Propolis wax	various	Pomegranate seed oil/ palm oil	(Fayaz et al., 2017)
Chocolate	EC 45 cP	-	Corn oil	(Li et al., 2021)
Ice cream	EC 10cP EC 20cP	10	High oleic sunflower oil	(Munk et al., 2018)
Bio-lubricating grease	EC	2	Castor oil	(Sánchez et al., 2011)
Bioactive delivery mechanism	EC 10cP EC 20cP EC 45cP	10-15.5	Canola oil	(O'Sullivan et al., 2017)

*0.76% of the total formulation

The applications listed in table 4 all use different concentrations of gelator and a variety of oil phases. This supports the theory that oleogels are very specific and should be formulated specifically for the desired application. More research is required into the interactions between other additives and active ingredients, specifically food additives. Hwang (2020) comments that careful thought should be given when selecting a gelator, so that the effect on sensory properties will be minimised. This is important for consumer acceptance.

2.5 Water-in-oil oleogel emulsions

Research into water-in-oil (W/O) oleogel emulsions is a novel area that builds on existing oleogel research. The primary objective is to investigate whether an oleogel containing dispersed aqueous droplets can be stable against phase separation and coalescence whilst maintaining gel properties. If successful, there is potential for hydrophilic and lipophilic nutrients to be incorporated into functional foods (Gao et al., 2021) and for oleogels to be incorporated into W/O emulsion-based foods.

Current research in this area is limited and primarily focuses on the development of wax-stabilised W/O oleogel emulsions. Wijarnprecha et al. (2019) found that rice bran wax (RBX) can stabilise W/O emulsions containing up to 50 w/w% dispersed water, and that its efficacy can be increased through the use of surfactants such as polyglycerol polyricinoleate (PGPR).

García-González et al. (2021) compared the effectiveness of surfactants GMS, GMO, GMP, and PGPR in assisting the formation and structure of a candellia wax (CW) W/O oleogel emulsion. The authors discovered that PGPR showed a higher emulsifying efficiency due to its ability to reduce interfacial tension and form a viscous film at the oil-water interface. PGPR was also very effective at reducing water droplet size. GMO and GMS enabled the dispersed water droplets to behave as aqueous fillers, in which case, the G' increased with increasing aqueous phase (AP). The opposite effect was observed in emulsions made with PGPR, where G' decreased with increasing AP. Monoglycerols formed a crystalline film at the oil-water interface preventing droplet-droplet interactions leading to coalescence and phase separation. In this situation GMP did not display the active filler behaviour seen in GMS and GMO. García-González et al. (2021) thought that this could have been due to the concentration of surfactant being too low, or negative interactions between GMP and the interface-active compounds (I.e. FAs, alcohols).

However Gao et al. (2021) found that surfactants were not necessary for an oleogel emulsion made with beeswax. This suggests that each gelator matrix is unique and surfactants may interact differently with depending on the gelator structure. A surfactant that improves one system won't necessarily improve a second system structured by a different gelator.

Wijarnprecha et al. (2019) and García-González et al. (2021) both agree that PGPR is very effective at lowering interfacial tension and reducing droplet size. However, monoglycerol based surfactants, such as GMO and GMS, are able to create interactions enabling the dispersed water droplets to act as active particles increasing G' as AP increases. Another point worth noting is that when the systems contained a higher percentage of water, the emulsion gels were found to become more shear-sensitive and have lower structure recovery (Wijarnprecha et al., 2019).

A foreseen issue with creating a W/O emulsion from an EC oleogel is that the gel point temperature is very high, and it is unsafe to add water to hot oil. Further research into lowering the gel point temperature could give more insight into how this could be feasible, or what the impact on gel stability will be if the water is added at a safe temperature. An area worth investigating is whether the EC will be able to stabilise the O/W interface as well as structuing the continuous phase.

2.6 Conclusion and recommendations

There has been significant research into oleogel systems over the past 30 years however there is still a lot more to be understood. Previous research has looked at different methods of oleogel structuring such as EC and plant waxes, each system appears to be structured by a different mechanism resulting in different physical and rheological properties. The advantage of this is that there is a lot of options when selecting an oleogel for application. Properties of oleogel systems can be improved with surfactants, and as the oil used in the system has a significant impact on the final gel. Thereore careful consideration and in-depth research is required when designing an oleogel system for a commercial application.

Research has shown promising results for the application of oleogels to food products, popular applications studied include processed meat products such as sausages and burger patties, bakery products such as cakes and breads, and emulsion systems such as spreads and ice cream.

Research into oleogel-emulsion systems is limited, current research on W/O oleogel-emulsion has primarily focused on structuring with plant waxes and there has been some success. Research into oleogel-emulsion systems structured by EC focuses on a O/W system. This highlights that there is space for more research into W/O oleogel-emulsion structured by EC as this success in this area would help with applying oleogels to W/O emulsion-based food systems.

3.0 Research Questions

The purpose of this study was to gain an understanding of oleogels and the critical factors affecting oleogel development.

- Experiments were conducted to gain a greater understanding of how EC oleogels and oleo-emulsions form, how they behave, and their response to stress.
- Oleogels have been developed using three different types of oil to understand how the lipid type influences EC oleogel formation and properties.
- Rheology was used for oleogel characterisation and measuring the limits of the system.
- The structure and stability of oleogels was investigated for the purpose of assessing the potential for use in food applications.

While characterising oleogels is not novel research, it is important to gain a thorough understanding of the subject matter before looking beginning oleo-emulsion research. Some researchers have conducted studies looking into the stability of an O/W oleo-emulsion, however, there is very limited research into EC W/O oleo-emulsions. A greater understanding of this subject could help with applying oleogels to W/O emulsion-based products such as ice creams, margarines, and cosmetic products.

4.0 Materials and Method

4.1 Materials

4.1.1 Ethylcellulose

EC was obtained in different viscosities (ETHOCEL 10cP, 45cP, and 100cP (fine particle grade)) from Colourcon (China). The viscosity (cP) of the samples was determined by the manufacturer by a 5 w/v% polymer solution in 80% toluene and 20% ethanol measured at 25°C.

4.1.2 Oil

All oil for this study was supplied by Bakels Edible Oils (NZ) Ltd. (New Zealand). Canola oil, sunflower oil and soyabean oil were stored at 5°C between experiments.

4.2 Sample preparation

4.2.1 Solubilising EC

Due to the ethoxy content of EC it is not readily soluble in oil or water, certain conditions are required for EC to dissolve. This study used a high temperature with agitation to solubilise the EC. The general method involved mixing oil and EC to form a cloudy solution at room temperature, as when the EC was added to pre-heated oil the powder tended to form insoluble lumps that would not disperse with just heat and stirring. The EC and oil solution was heated on a magnetic hot plate with a temperature monitoring probe. A magnetic stirrer was used to stir the solution while heating. The dispersion of EC into oil was observed as the solution changed from cloudy white to light yellow and an increase in viscosity.

4.2.2 Gelation of oil

Gelation began with the EC dissolving into the oil, a noticeable increase in viscosity was also observed at this time. The viscosity of the solution continued to increase as the system reached 140°C. The solution was held at this temperature for 10 minutes to ensure maximal viscosity increase while minimising oxidation. After this, the solution was left to cool at room temperature which allowed solution to set.

The transition from a viscous oil to a solid occurred over a temperature range of 90-130°C. The exact point of the phase change was difficult to identify because a skin would often form on the

surface of the gel, while the core would still be molten. The solution would set near-instantly as the molten gel was poured into the mold which made this very delicate process.

4.2.3 Preparation of W/O oleo-emulsions

Limited research was available on creating W/O oleogel-emulsions and the information that was available focused on systems structured by other gelators like plant waxes. The challenging factor was the high temperature required for EC to dissolve. Early trials were unsuccessful as the water was added at 90°C but quickly evaporated in the viscous oil solution and a foam-like phenomenon occurred. While this biphasic system is interesting in its own right, it was not the objective of this study. An emulsion was successfully formed when the EC oleogel was pre-set and cooled before emulsification. Water was added to the gel at room temperature and shear was applied using an ultra-turrax high shear overhead mixer. The amount of time required for a stable emulsion to form was dependent on the volume of solution, but for a 100-gram sample two minutes at 20,500 rpm was sufficient.

4.3 Experimental Methods

4.3.1 Thermal behaviour analysis using DSC

5-10mg samples were weighed into a Tzero pan and sealed with a Tzero hermetic lid (TA Instruments). EC powder was used for powder-only trials. For the EC and canola oil trial, the 10% solution was prepared by mixing 10 w/w% EC with canola oil to form an opaque cloudy solution. No materials were heated prior to testing. The DSC model was a Q2000-2960 (Alphatech Systems Limited) and the data analysis was performed using Universal Analysis (TA Instruments Universal analysis 2000). An empty pan was used as a reference. For the first trial with EC 10cP, the starting temperature was set to 25°C and then the system was heated to 200°C at a rate of 5°C per minute. For all following trials, a second heating and cooling stage was added to test for hysteresis. After being heated to 200°C, the sample were then cooled at a rate of 10°C per minute back to 25°C then reheated at 5°C per minute back up to 200°C. Each grade of EC was tested in triplicate to ensure the reliability of the results. This methodology was based on a study by Davidovich-Pinhas et al. (2015).

4.3.2 Material behaviour of EC oleogels

Three types of oil were used in this study including canola oil, sunflower oil and soyabean oil. Gels were prepared in concentrations of 6%, 8%, and 10% w/w EC. The oleogel solution was prepared as detailed above, then poured into round molds with a 28mm diameter. Samples were cooled to room temperature then and left in a chilled storage room set at 5°C for 24 hours.

For rheological testing a torque-controlled rheometer (MCR302, Anton Paar, Saint Laurent, QC, CA) equipped with a temperature control unit and a serrated parallel plate geometry with a 20mm diameter. Three common sweep tests were used to assess the samples. Firstly, a strain sweep test where the strain was set to 0.001-1000% with a fixed frequency of 1Hz. For the frequency test a frequency range of 0.1 – 10Hz was used for consistency a strain of 0.1% was also applied to ensure the sample was within the LVR range. Lastly, a temperature sweep monitored the changes in gel properties over a temperature of 20°C - 80°C. A strain was applied at a fixed rate of 0.1% and frequency set fixed at 1 Hz to ensure the samples were being tested within the LVR. The temperature was controlled at 20°C across all testing (except where stated). This methodology was based on a study published by Ashkar et al. (2019).

The next rheological test followed a different structure, the three interval thixotropy test (3iTT) was used to investigate the structure-recovery properties of oleogels. Viscosity was measured as a function of time under alternating cycles of shear stress. One test was made up of three 600-second cycles, each changing the level of shear stress from low (0.1/s) to high (10 1/s) and back to low (0.1/s).

4.3.3 Structure and stability of oleogel-emulsions

4.3.3.1 Effect of gelator concentration, water concentration and shear on emulsion stability

Emulsions were made from a pre-set canola oil gel using either 3 or 5 w/w% EC, 20 or 50 w/w% water, and an ultra-turrax was used for shear and a low and high shear setting was used for comparison. The low setting was 6800 rpm for 2 minutes and the high setting was 20500 rpm for 2 minutes. Table 6 displays the sample number and corresponding sample composition.

Micrographs were taken using an Olympus BX53 system microscope connected to a PC with photo taking software.

Table 4 Oleogel-emulsion sample composition and emulsifying shear rate for the stability test.

Sample	Water (w/w%)	EC (w/w%)	Shear
1	20	3	Low
2	20	3	High
3	20	5	Low
4	20	5	high
5	50	3	Low
6	50	3	High
7	50	5	low
8	50	5	high

4.3.3.2 Effect of storage temperature on emulsion stability

A second experiment was conducted following a similar method that investigated the effect of temperature on emulsion stability. Four emulsions were prepared with 20 w/w% water and 3 w/w% EC. An ultra-turrax was used for shear on a setting of 20500 rpm for 2 minutes. Then samples were stored at different temperatures for 96 hours and left at room temperature for a further 24 hours before being visually inspected under a microscope. Micrographs were taken using an Olympus BX53 system microscope connected to a PC with photo taking software.

4.3.3.3 Visual stability test

3 w/w% and 5 w/w% oleogels were prepared as previously described. Once set, water and 0.5ml of both 1% Red O and 0.1% Methylene blue were added to the gels. The emulsions were blended to mix in the dye and water for 6 minutes each using a ultra-turrax on setting 20500 rpm for 6 minutes. A longer amount of time was used for these samples as a larger volume of

sample was being prepared. After mixing, three 10ml samples were taken from each emulsion and put into glass Klimac tubes before being covered and left at room temperature.

Figure 3 Visual stability test on day 1 showing 3 w/w% (left) and 5 w/w% (right) oleogel emulsions.

4.3.3.4 Rheological behaviour of EC oleogel emulsions

EC and canola oil was weighed out, mixed thoroughly, and heated to 150°C for gelation. Next, the gels were left to set at room temperature (25°C) for a minimum of 24 hours before emulsifying. Gels were made with a concentration of either 3 or 5 w/w% EC and 20 w/w% water to compare the effect of gelator concentration on the rheological properties of the emulsion. Table 5 displays the gel composition and shear used for emulsification.

Table 5 Oleogel-emulsion sample composition and shear rate used for the strain-sweep test.

Sample	EC (w/w %)	Water (w/w %)	Shear (rpm)
1	3	20	20500
2	5	20	20500

The emulsions were split into two samples, sample 1a and 2a were taken for testing on day 1, and sample 1b and 2b were stored at 5°C whilst they waited for testing on day 7. This was to assess whether the viscosity of the samples changed during storage.

The same parallel plate geometry was used for oleogel-emulsion testing as was used for the oleogel testing.

5.0 Thermal behaviour of EC

5.1 Introduction

Differential scanning calorimetry (DSC) measures changes in enthalpy that occur with increasing or decreasing temperature (Cisse et al., 2021). Enthalpy is measured as heat flow (W/g) and is plotted as a function of temperature to give a thermal profile. An endothermic change in enthalpy is heat being released into the system when polymer bonds are being broken during a glass or melting transition. An exothermic shift absorbs enthalpy from the system when bonds are formed such as during recrystallisation into a secondary or tertiary structure. This study compares the thermal profile of different grades of EC and an EC and canola oil gel. Similar studies have been conducted by researchers such as Davidovich-Pinhas et al. (2015), Ahmadi (2020) and Fu (2020).

The molecular weight of EC influences the polymer characteristics, particularly thermal transition temperature (Davidovich-Pinhas et al., 2015). The higher viscosity is a result of increasing the carbon chain length which also increases the molecular weight of the sample (Ahmadi et al., 2020). Longer carbon chains are stronger and require more energy for bonds to be broken, i.e. during a glass transition, and hence the thermal transition temperature of EC increases with increasing viscosity (10cP < 45cP < 100cP).

The thermal events of interest are the glass and melting transition while heating, and recrystallisation and vitrification transition on cooling. A glass transition is where amorphous areas of a polymer use energy to get rid of strong inter-molecular bonds so that the material can change from a glassy to a rubbery state (Ma et al., 2021). Glass transitions generally occur between 130 - 150°C (Davidovich-Pinhas et al., 2016; Fu et al., 2020; Giacintucci et al., 2018)

and, along with melting peaks, demonstrate that EC has a semi-crystalline structure (Ahmadi et al., 2020). EC can melt at temperatures between 165-173°C and decompose at temperatures over 200°C (Ahmadi et al., 2020).

By collecting a thermal profile of each EC viscosity grade, the results can be compared against those given by literature to see if there are any differences. Through understanding the thermal behaviour of EC, a more accurate set of parameters regarding the minimum temperature required for sufficient gelling to occur, and the maximum temperature for heating to minimize oxidation and the degradation of EC can be set for future trials.

5.2 Results

This thermal analysis was conducted using EC powder, and an EC and canola oil mixture. The EC and canola oil was mixed prior to testing and a pipette was used to transfer a sample into the DSC pan. The purpose of this was to observe the thermal profile of EC powder and see what changes occur when canola oil is added. While it was not tested in this experiment, previous studies by Davidovich-Pinhas et al. (2015) and Adili et al. (2020) found that canola oil does not show any thermal behaviour on a DSC thermogram, and therefore it is assumed that all thermal events occurring are due to the presence of EC. DSC thermogram data is shown in figure 4. It can first be noted that there appears to be a thermal event between 60-80°C, and which is observed during the first temperature cycle but is not visible for the second heating stage. This suggests that there is an impurity present that undergoes an irreversible transition, and the curve is not relevant for the purposes of this work.

5.2.1 Influence of EC viscosity

The thermal events appear to become more significant (i.e., a larger change in enthalpy) with increasing EC viscosity. This was expected as we know that a higher viscosity grade EC has longer carbon chains which require more energy to be broken (Davidovich-Pinhas et al., 2016; Fu et al., 2020; Gravelle et al., 2018). It was also expected that the glass and melting transitions would occur at a slightly lower temperature for the 10cP and 45cP sample compared to the 100cP sample, as a longer carbon chain should require more thermal energy for thermal events to occur as there are more bonds to be broken and reform during phase transitions.

5.2.2 Glass and melting transitions

The glass transition is difficult to identify on all the thermograms. Traditionally, a glass transition is displayed as a stepwise endothermic drop in enthalpy which occurs as the bonds are broken indicating that the polymer has changed from a glassy to rubbery state (Ma et al., 2021). The glass transition for the EC powder was approximately 130.9°C, 126.5°C, and 136°C for 10cP, 45cP, and 100cP respectively. For the EC and canola oil gel, it appeared at approximately 137°C.

It is unlikely that the 45cP sample was the first to reach the glass transition as it should have been the 10cP sample. However, as the glass transitions are not easily identified on the thermograms then these values should only be taken as a general figure. The melting transitions were also very difficult to identify. An endothermic peak occurred consistently around 180°C for all samples. It has been assumed that this is a melting transition as it is consistent across the different samples, and it lines up with previous studies.

EC 45cP and 100cP samples both displayed a thermal event that resembled the powder recrystallizing into a secondary structure at approximately 176°C. This was not present in the 10cP sample as there was no second heating cycle, and it was also not present in the EC and canola oil sample as it is believed the solute-solvent interactions occurring during the glass transition prevent EC from recrystallizing into a secondary structure (Davidovich-Pinhas et al., 2015).

5.2.3 Comparison of first and second thermal cycles

The profiles of the first and second heating cycles show significant differences. For example, there is an exothermic peak occurs during the first heating cycle that is not present during the second. This suggests that the compound responsible is no longer present. Ma et al. (2021) also found an unexpected exothermic peak which replaced the glass transition at 136°C which was attributed to oxidation, whilst the peak observed here occurs at higher temperatures than what Ma observed. It is still possible oxidation could have an influence on the thermal profile considering that EC is known to melt above 165°C and degrade at temperatures over 200°C.

Davidovich-Pinhas et al. (2016) tested for thermal hysteresis by adding a second temperature cycle, and the same methodology was used here. The glass transitions in the secondary heating stage occur at a lower temperature compared to the first heating stage (see figure 4 (c) and (d)), but there does not appear to be any significant difference between the primary and secondary melting transitions.

Ahmadi et al. (2020), Davidovich-Pinhas et al. (2016), and Fu et al. (2020) put this shift down to the presence of local inhomogeneities in the powder due to the presence of moisture which was evaporated during the first heating cycle. However, the peak in question occurs on the 10cP, 45cP, and 100cP powder thermograms at roughly 150-170°C which makes it unlikely to be caused by the presence of moisture.

The thermal events in the second heating cycle are very similar to those displayed by Davidovich-Pinhas et al. (2015). Both results show clear differences between the powder glass transition and the EC and canola oil glass transition. Davidovich-Pinhas et al. (2016) commented that in the presence of oil the thermal transition seems to include the glass transition of powder superimposed on an endothermic transition involving latent heat. It appears that the polymer glass transition is followed by chain dissolution which includes interactions between the solute and solvent i.e., endothermic heat of solution. The authors also explain that this endothermic thermal event can be described by the Flory-Huggins free energy of mixing theory, where the dissolution of two components is governed by the negative energy of mixing which promotes interactions between the two components in the mixture.

This endothermic peak can be seen in figure 4 during the cooling cycle of (b) and (c) which does not appear in (d). This suggests that the semi-crystalline structure of EC does not reform when EC is in solution with canola oil. The absence of any thermal transitions during the cooling and secondary heating stage suggests that, as previously mentioned, because of the solute-solvent interaction occurring as part of the gelation mechanism, EC is no longer able to reassemble into a secondary structure. This behaviour was also observed by Davidovich-Pinhas et al. (2015).

If the presence of a secondary structure is desirable, then the incorporation of a low molecular weight organogelator (LMOG) into the gelation mechanism could prove beneficial. Fasolin et al.

(2018) provide a good comparison of the effect of sorbitan and glycerol based LMOGs on the different edible oil structures, including an analysis of their thermal behaviour through the use of DSC. The use of stearic acid and stearoyl alcohol with EC oleogels has also been examined by Gravelle et al. (2016). It was proven that EC interacts with the surface-active molecules and that the chemical potential ($\Delta\mu$) between the solvent and stearic acid or stearoyl acid can affect the thermal profile, specifically, the temperature at which melting and crystallization occur.

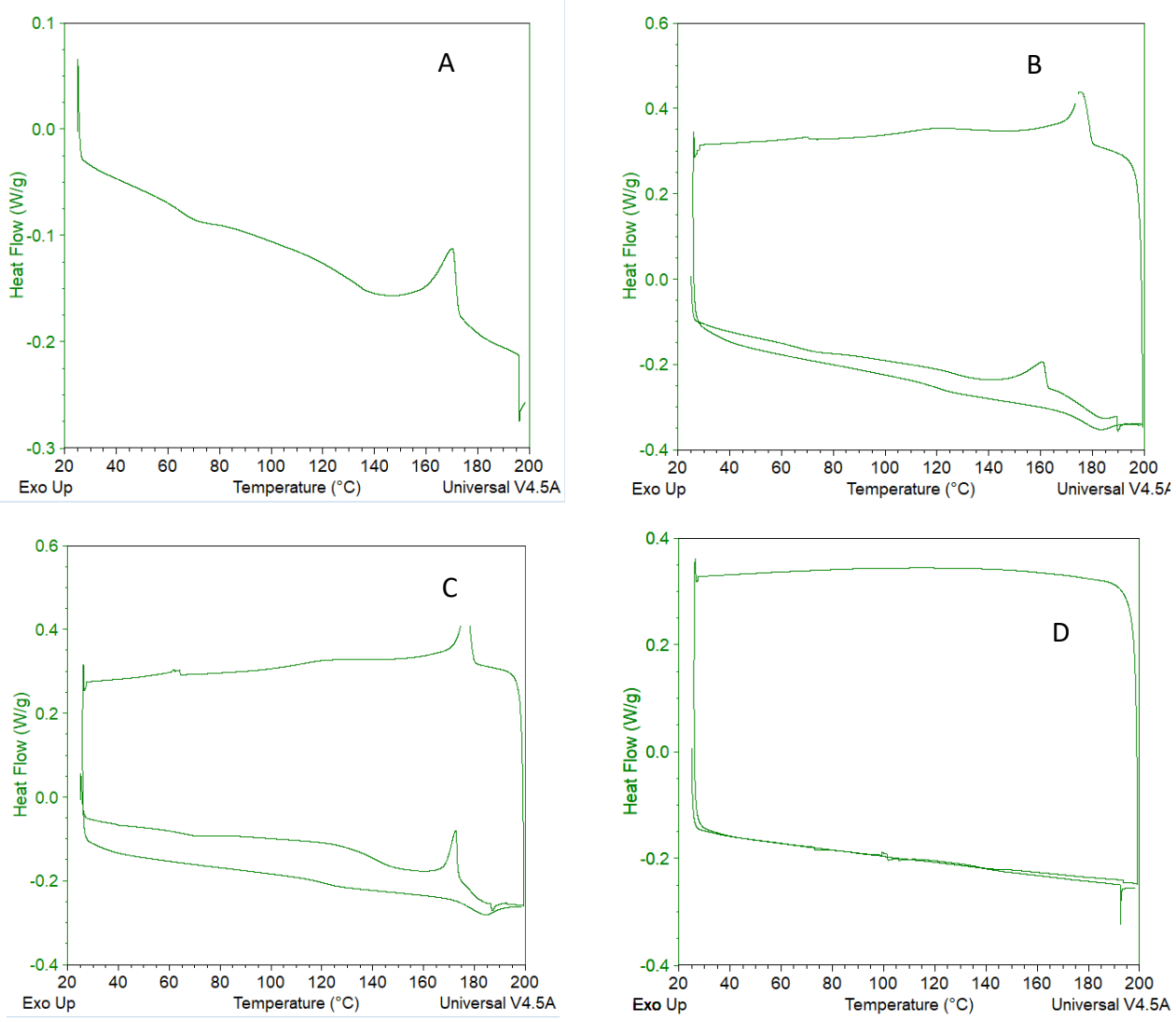


Figure 4 Comparison of EC thermal profiles with varying viscosities, and therefore differing carbon chain lengths. (A) 10cP, (B) 45cP, (C) 100cP FP, and (D) 100cP FP 10 w/w% with canola oil.

Lastly, the presence of the 150-170°C exothermic peak was troubling and after a more general look into the DSC testing of EC powder, it was suspected that the peak could be due to the presence of antioxidants. After an email to the supplier, it was confirmed that ETHOCEL contains < 150ppm of the antioxidant propyl gallate. It is a very small amount, and it is unknown if this could explain the unusual result. A way of testing this would be to acquire a second sample of EC from a different supplier for testing. EC is difficult to source in New Zealand, especially during the COVID-19 pandemic, so this was not possible at the time of testing.

5.3 Discussion

The 100cP EC samples had the highest apparent T_{gel}. This was expected due to the carbon chain length increasing with viscosity grade requiring more energy (heat) for the glass transition to occur. There was also no significant difference between the EC powder, and EC and canola oil mixtures which was also expected as previous studies have proven that canola oil does not have any thermal transitions of its own.

It was interesting to see how the difference between the EC powder and EC and canola oil thermal profiles, and how the exothermic transition on cooling no longer appeared indicating that the gel mechanism occurring EC and canola oil inhibits EC from recrystallizing into a secondary structure. If re-crystallising and forming a secondary structure is desirable, then it is recommended that surfactants are incorporated into the gel.

When available, further samples of EC should be acquired and tested to compare the results with those presented in the literature and those found in this experiment. It is possible that environmental factors such as oxidation or moisture could have influenced the thermal profile due. However, the unexpected thermal events were relatively consistent across all three samples (10cP, 45cP, and 100cP) which indicates that it could be a minor compound, such as an antioxidant, causing these results. It is recommended that this temperature sweep rheology experiments are run to follow up from this study to analyse the gel properties as a function of temperature.

6.0 Material behaviour of EC oleogels

6.1 Introduction

Understanding how a material will respond to force is critical for food processing. The two primary categories of fluids are Newtonian and non-Newtonian. Newtonian fluids follow Newton's law of viscosity which means that viscosity is constant and will not change when forces are applied (Nakayama, 2018). In food processing, a materials response to force is very important as this is a critical consideration when designing a process. Common mechanical forces a food may encounter include pumping and stirring. Non-Newtonian fluids demonstrate changes in viscosity when force is applied. These types of fluids can be further categorized into pseudoplastic fluids, Bingham fluids, and dilatant fluids.

Pseudoplastic fluids are shear-thinning, where viscosity decreases with increasing shear, and dilatant fluids are shear-thickening where viscosity increases with increasing shear. Bingham fluids have solid-like behaviour until a critical force is applied then viscosity will quickly decrease and level out into a more constant flow (Nakayama, 2018).

Fat texture and functionality are a result of rheological characteristics, for example, fat spreadability arises due to plastic flow (Marangoni et al. 2020). The rheological properties of fat-based products are determined by the structural features of the fat crystal network. Martins et al. (2018) observed that longer chain triglycerides displayed improved viscoelastic properties compared with medium chain triglycerides, this was assumed to be due to the different conformational structures created by the carbon chains.

Foods that display time-dependent shear-thinning behaviour exhibit thixotropic flow. Most foods that display this behaviour are heterogenerous systems containing a very fine dispersed phase. At rest, the particles or molecules are linked together by weak forces but when the hydrodynamic forces are sufficiently high, the interparticle linkages are broken causing a size reduction of the structural units and decreasing the resistance to shear.

Materials possessing both viscous and solid properties are known as viscoelastic materials. These types of materials typically respond to stress or applied force with structure

deformation or flow (Prasad & Bhatt, n.d.). A rheometer is used to characterise the behaviour of a viscoelastic material by collecting and presenting data on the way a fluid (or semi-fluid) responds to an applied force. Common variables include frequency, time, strain, stress, and temperature.

Two parameters used to describe viscoelastic behaviour are the storage modulus (elastic, G'), and loss modulus (viscous, G"). G' is a measurement describing the structure of a material, and G" describes the materials response to a force in terms of viscosity or flow properties (Hill, 2019). Complex modulus, G*, is a measure of overall stiffness that considers both viscous and elastic behaviour (Hill, 2019). Liquid-like behaviour is observed when G" > G', whereas solid-like behaviour is observed when G' > G". When G" = G', this is referred to as the 'gel point' where the material is equal parts liquid-like and solid-like (Gravelle et al., 2018)

Gels are a complex state of matter which blur the lines between a liquid and a solid. This category is a spectrum of materials that display both solid-like and liquid-like properties. A materials ability to deform and flow is described through rheological principles (Hill, 2019) and this chapter will apply these principles to oleogels.

6.2 Results

It was decided to proceed with solely testing to 100cP FP EC as this created harder gels than the 10cP and 20cP EC. As explained earlier, this occurs due to higher viscosity grade (100cP) having a higher molecular weight and therefore longer carbon chain. Therefore, the 100cP EC can form a stronger gel matrix as there is more junction points for hydrogen bonding.

6.2.1 Strain sweep

A strain sweep was first conducted to measure the storage (G') and loss (G") moduli as a function of time. Figure 5 shows that the moduli were relatively unaffected by shear before the critical strain was reached at 1%. As strain continued to increase past 1%, the moduli began decreasing which indicated that the gel was no longer in the linear viscoelastic region (LVR). G" > G' observed in figure 5 indicates that the gel was failing. Testing within the LVR is important, as within this range the stress response does not depend on strain or frequency inputs. The

moduli of the 10 w/w% EC oleogel was higher than the 8 w/w% EC oleogel, indicating that the 10 w/w% oleogel had a stronger gel network.

Interestingly, there doesn't appear to be a significant difference in gel strength between the samples made with canola oil, sunflower oil or soyabean oil. As previously mentioned, past studies claimed that the type of oil would have a large impact on gel strength, however this was not the case for this study. The oils used here all have high levels of unsaturated fatty acids which may explain why there was such an insignificant difference. If oils such as palm and coconut were used, then the researcher may expect to see a much larger difference in gel strength.

All further testing was carried out below the critical strain. The results for 10 w/w% SBO have been purposely excluded from this graph due to data errors.

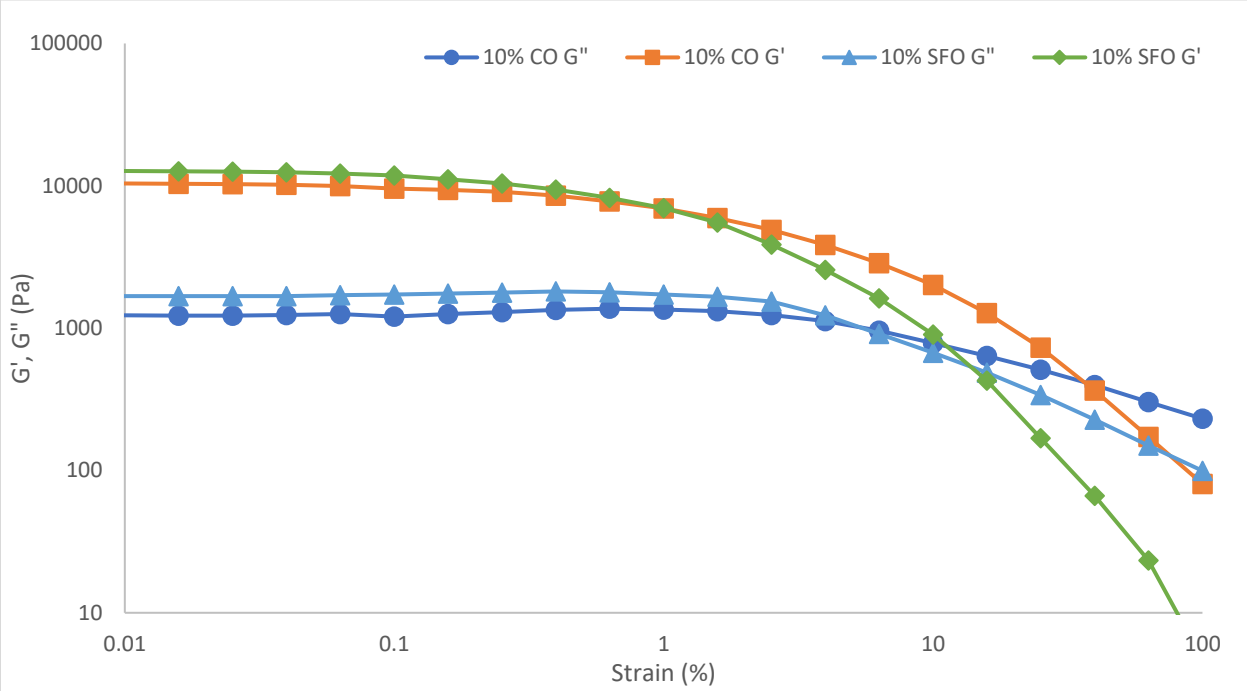


Figure 5 Strain sweep test of 10 w/w% EC oleogels at a fixed frequency of 1 Hz at 20°C.

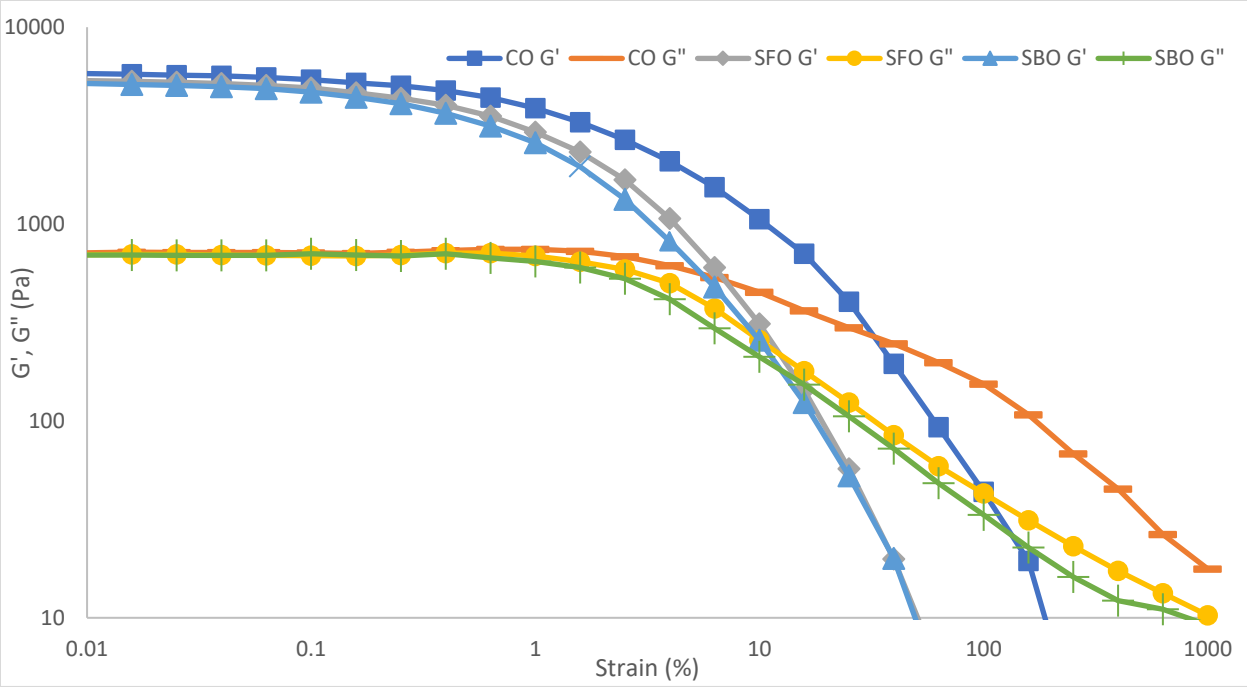


Figure 6 Strain sweep test of 8 w/w% EC oleogels at a fixed frequency of 1 Hz at 20°C.

6.2.2 Frequency sweep

The results show a linear trend where G”> G’ demonstrates solid-like behaviour that does not fail within the tested frequency range. The behaviour shown is typical of a solid fat (G” > G’). An interesting observation is that the 10 w/w% gels are displaying a weaker gel behaviour than the 8 w/w% oleogel. This is indicated by the lower moduli which can be seen in figure 7 for the 8 w/w% oleogels and figure 8 for the 10 w/w% oleogels and is summarised in table 7.

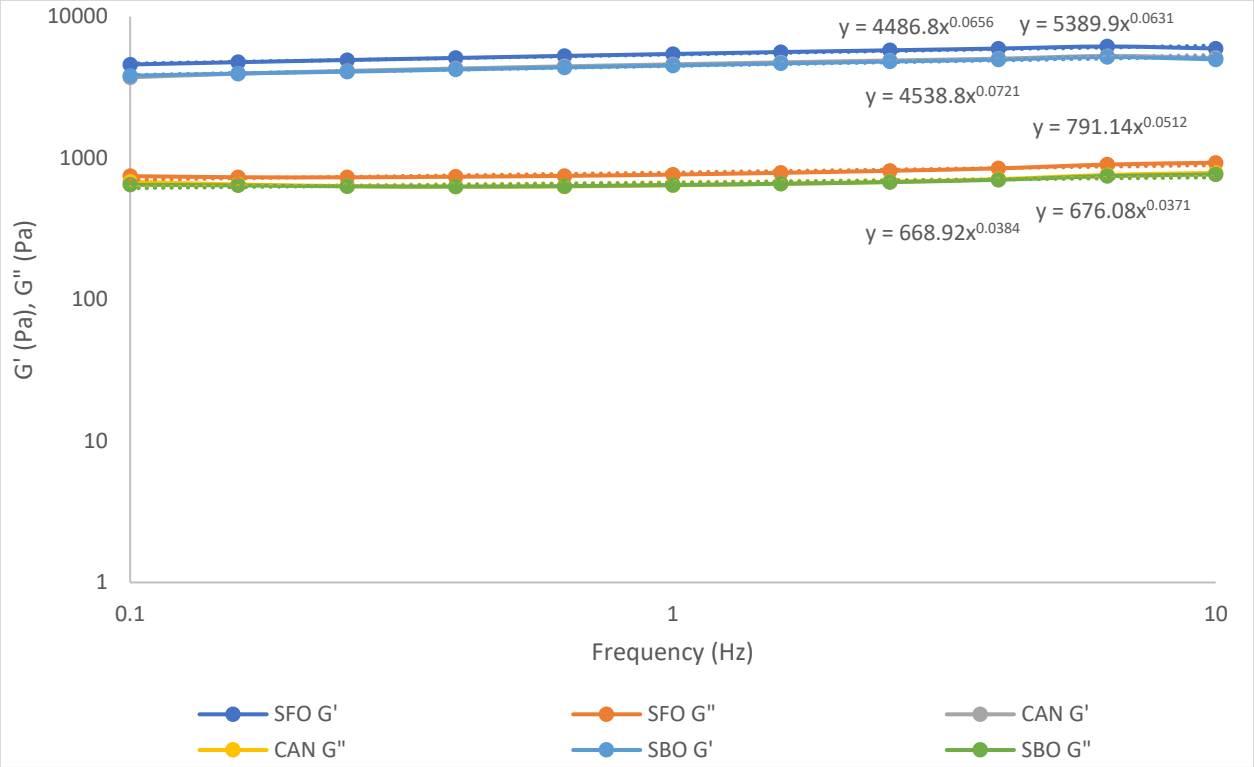


Figure 7 Comparison of G" and G' behaviour as a function of frequency for three oleogels made with 8 w/w% EC and either canola oil, sunflower oil or soyabean oil.

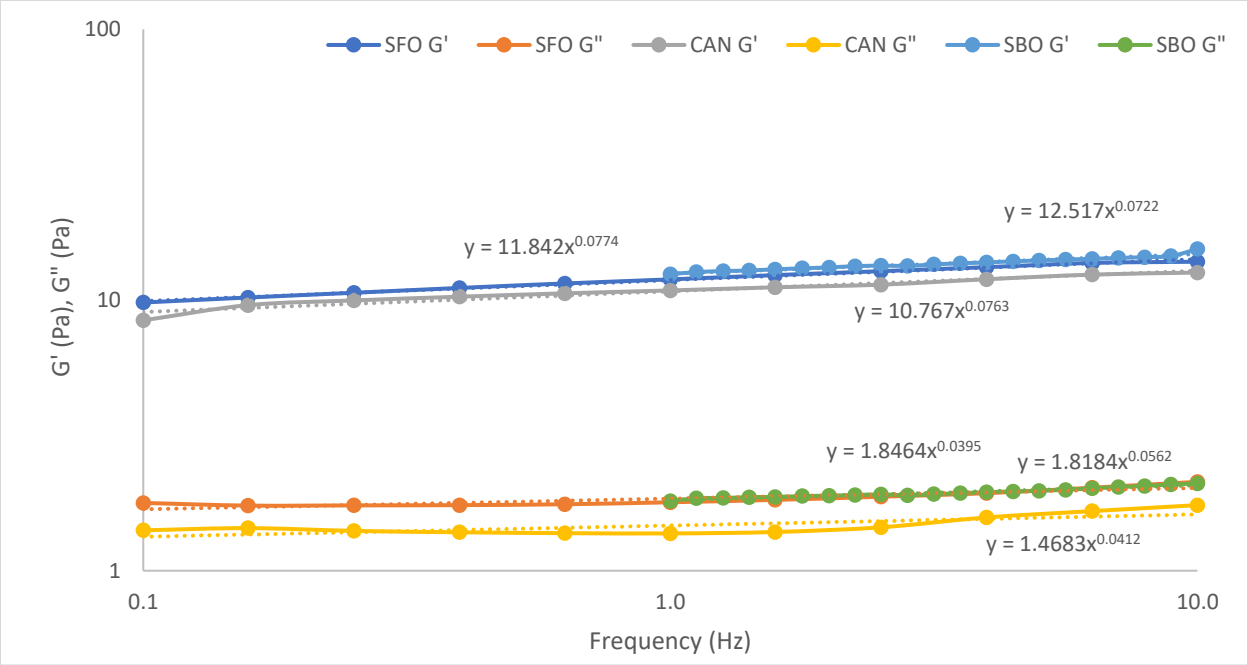


Figure 8 Frequency sweep fitted with a power law model comparing the G'' and G' as a function of frequency for three gels made with 10 w/w% EC and either canola oil, sunflower oil, or soyabean oil.

The power law model gives values for the Y axis intercept and the slope of the trendline so that the magnitudes can be compared.

$$Power\ Law\ Model\ = kx^n$$

Where k is the slope and n is the intercept.

This model was applied to the frequency sweep graphs in figure 7 and 8. The values for k and n are presented in table 7.

Table 6 Magnitudes of slope (K', K") and intercept (n', n") from the linear regression of Log Frequency versus Log G" and Log G' of oleogels made with 8 w/w% or 10 w/w% EC and various oils.

	G' (Pa)		G" (Pa)	
Sample	K'	n'	K"	n"
8 w/w% SFO	5390	0.0631	791.1	0.0512
8 w/w% CO	4539	0.0721	676.1	0.0371
8 w/w% SBO	4487	0.0656	668.9	0.0384
10 w/w% SFO	11.84	0.0774	1.846	0.0395
10 w/w% CO	10.77	0.0763	1.468	0.0412
10 w/w% SBO	12.52	0.0722	1.818	0.0562

6.2.3 Temperature sweep

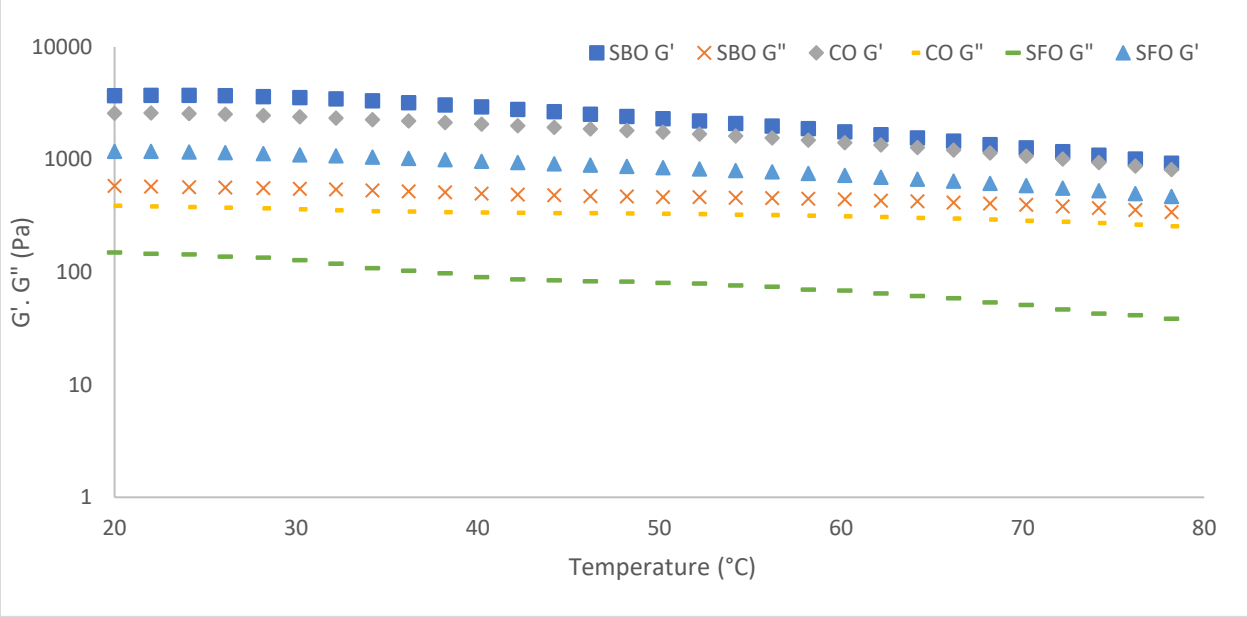


Figure 9 Temperature sweep between 20°C and 80°C for 8 w/w% EC oleogels made with soyabean oil, sunflower oil, or canola oil.

Figure 7 demonstrates the thermal resistance of EC, the moduli appear to gradually decrease over the demonstrated temperature range, but no significant changes occur. The temperature of the experiment was not high enough to observe the gel transition point where G'= G". Due to the limits of the machines, the samples were not able to be retested in a higher temperature range.

6.2.4 Thixotropy

A 3 interval thixotropy test (3iTT) was conducted to understand more about the samples ability to recover viscosity after the structure has been broken down. A decrease in viscosity is observed during the first low shear interval (0.1 1/s) which indicates thixotropic behaviour. This is likely due to a partial breakdown of the linkages holding the EC matrix together which reduces the viscosity as the liquid oil can move more freely within the structure. The next shear interval is higher (10 1/s), resulting in a large decrease in viscosity and the samples display weak gel behaviour. The third interval which repeats the first low shear setting (0.1 1/s) shows partial structure reformation indicated by a large viscosity increase. The structure does not fully recover, demonstrating that some of the gel structure has deformed irreversibly during the high shear. It is important to keep in mind that the cycles were only 600 seconds long and that the structure may continue to recover with time. These results can be seen in figure 10. The 6 and 8 w/w% gels were chosen for testing as they were the most liquid-like gels that could still hold their shape and be transferred onto the testing apparatus without being damaged.

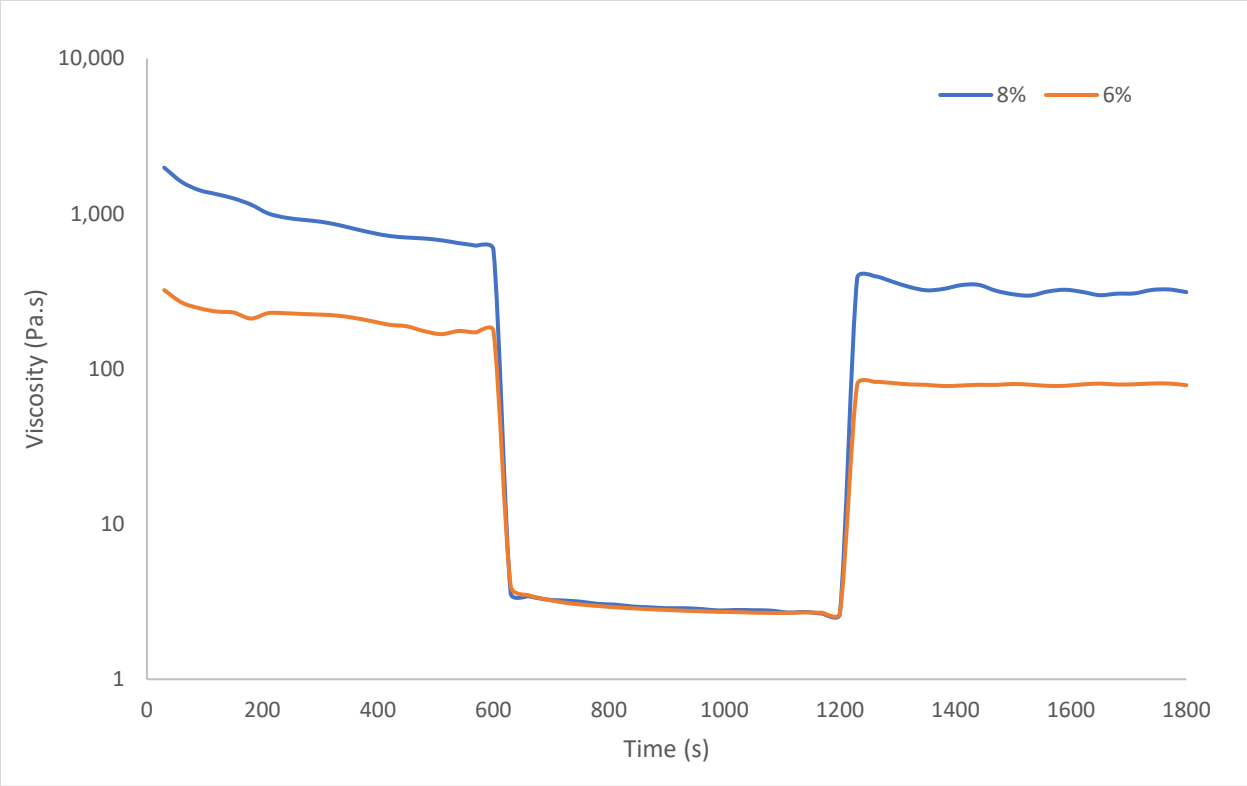


Figure 10 Oleogels displaying thixotropic behaviour after going through three shear cycles, a 6 and 8 w/w% EC oleogel were tested to compare the effect of gelator concentration on the ability to recover viscosity after shear.

6.3 Discussion

The oleogels displayed shear thinning behaviour across both the sweep and thixotropy tests which was observed by a decrease in viscosity with increasing shear rate. Changes in viscosity due to the application of shear provides important information about a materials processing and performance. This is important for food manufacturers if oleogels are going to be used as an ingredient in food applications, as non-newtonian fluid behaviour can cause issues during processes such as stirring, dispensing, and pumping.

The average G' and G" are related to the solid-like (elastic) and liquid-like (viscous) characteristics of the material. The typical behaviour for fats is G' > G'' which indicates that more energy is being stored rather that dissipated, G' usually sits between 10^5–10^6 Pa and has low-frequency dependence, which are characteristics typical of soft viscoelastic solids

(Marangoni et al. 2020). The results here are similar with G' > G", and G' sitting lower at approximately 10^4. When G" > G' is observed above the critical strain, this shows that the material is behaving more like a solid than a liquid. These results agree with those published in a study by Moon et al. (2021) which looks at the LVR of carnauba wax-canola oil oleogels.

Even though the oleogels do not appear to be as solid as typical fats, this should not have too large of an impact if applied to a food application. The potential for an oleogel to be incorporated into the fat phase of a food product as a substitute or partial substitute is promising as oleogels can demonstrate solid-like behaviour at higher temperatures than typical solid fats, this was demonstrated by the thermal resistance seen in the temperature sweep test. Applications where this could be useful include spreads and ice creams, particularly for markets with a hot climate such as Asia.

7.0 Structure and stability of EC oleogel-emulsions

7.1 Introduction

Condiments, ice cream, spreads, and milk are all emulsion-based food applications. Emulsions consist of a dispersed and continuous phase, which can be oil-in-water (O/W) or water-in-oil (W/O) with a typical particle size range of 0.01-10μm (Rao, n.d.). Emulsion stability is a common issue with these types of products, as if the emulsion breaks the product is often less appealing to consumers and it may appear as the item has "gone off". Improving the stability of an emulsion can increase the shelf life of a product. Research on emulsion stabilisation is exhaustive, however, all systems vary and require individual research and development so new developments are always popular. Oleogel-emulsions is a novel area of research, and to the authors knowledge, research on EC stabilised oleogel-emulsion systems is very limited. Current research in this field has focused on O/W stabilised emulsions whereas this study looks at the possibility of creating a W/O emulsion. The purpose is to look at new approaches for margarine type products that don't require coconut or palm oil. An EC oleogel system was selected due to the unique gelling ability and temperature stability, as seen in the previous chapters. This chapter aims to test if an EC oleogel can maintain the gelled properties of an oleogel whilst stabilizing a dispersed aqueous phase of up to 20 w/w% of the sample. The water content of margarine is approximately 15-20 w/w%, which is why this water content was selected for the trials.

7.2 Results

7.2.1 Forming an oleogel-emulsion

Initially there was some difficulty forming a stable emulsion due to the high temperature required for gelation. The ability to form a stable emulsion was dependent on the temperature of the oleogel at the time of emulsification. Mixing the oil and water phases near the gel set point (80- 90°C) would cause the water phase to evaporate and create a foam-like biphasic structure. To create an oleogel-emulsion, the gel needed to be set and cooled to room temperature first. Then by adding water and applying shear a stable emulsion would form. The

high shear required for emulsification does break up the gel structure and reduce viscosity, this was clear as the sample now had a similar texture to a thick yoghurt, it is less rigid and flows.

7.2.2 Effect of shear, water concentration and gelator concentration

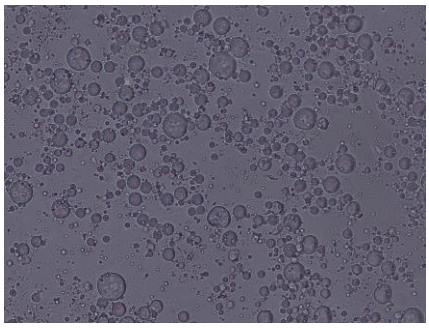
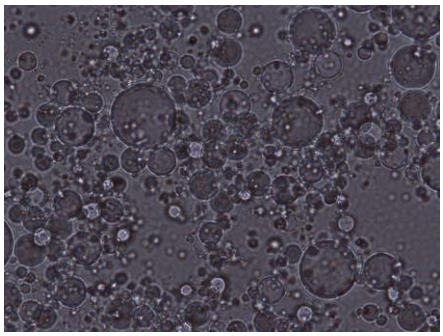
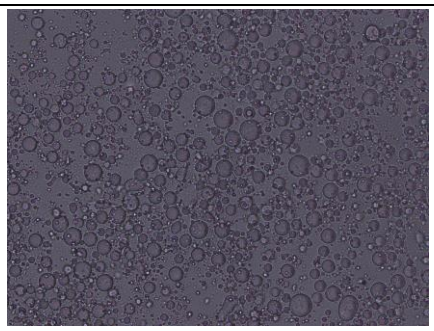
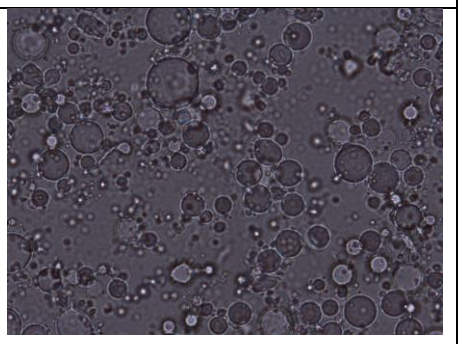
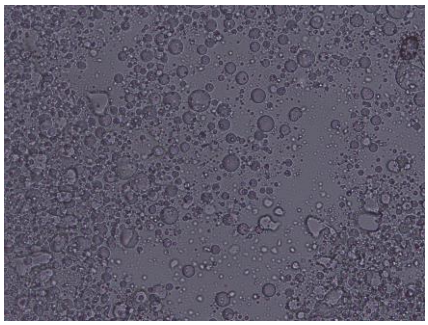
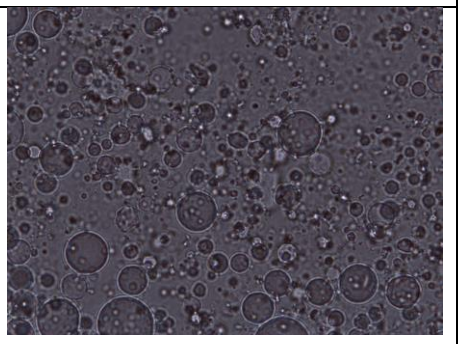
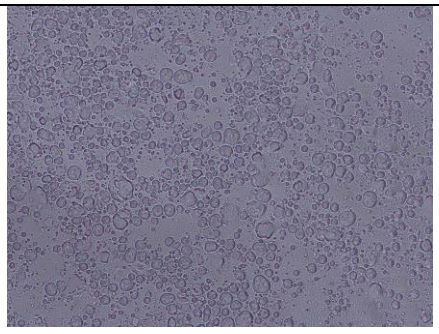
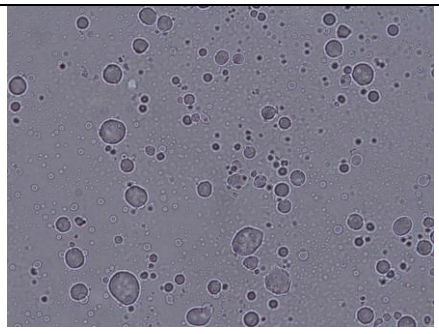
Samples 7 & 8 contained 50 w/w% water and 5 w/w% EC. These were the only samples that did not form a stable emulsion. They had an excess of water which would not mix into the solution. Sample 7 was made with low shear and sample 8 had high shear but this did not appear to affect the results. Photos of each sample can be seen in table 8.

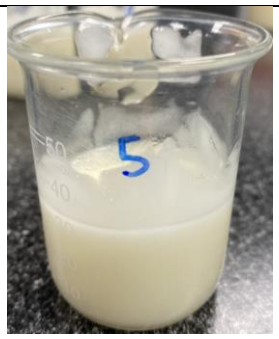
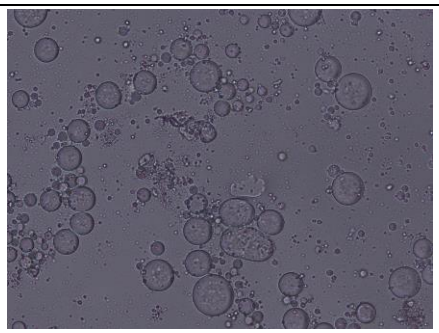
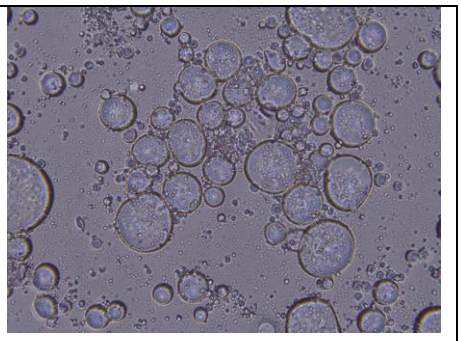
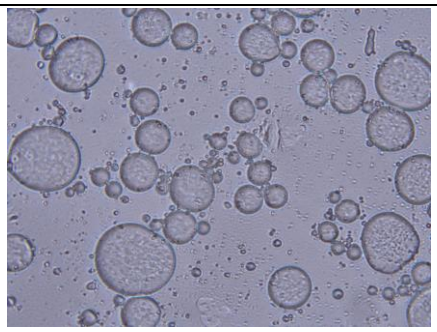
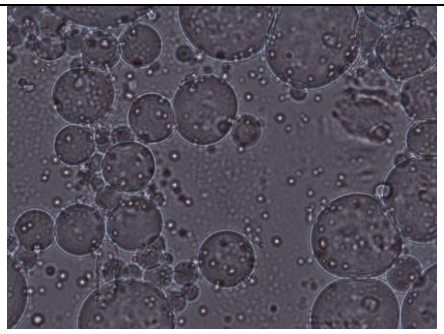
Samples 5,6,7 and 8 all had water droplets that were considerably larger than samples 1,2,3 and 4 which can be seen in the micrographs in table 7. These samples had a higher water content of 50 w/w% and a higher water content typically corresponds to larger water droplets which indicate a lower emulsion stability. Samples 5&6 (5 w/w% EC) appeared more stable than 7&8 (3 w/w% EC) which could be due to a higher gelator concentration.

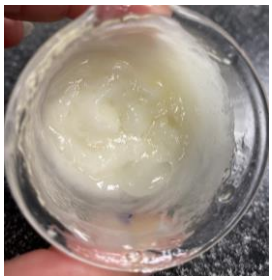
It is difficult to tell visually whether the low or high shear made a difference, but samples 2 and 4 appear to have the smallest water droplet particle size. This indicates that these were the most stable emulsions. Sample 2 was made with 3 w/w% EC, and sample 4 was made with 5 w/w. Both emulsions had a 20 w/w% water concentration and used high shear.

The images taken during microscopy (table 7) suggest that the droplets are covered with particles. The microparticles of EC oleogel may be able to stabilise the surface of the droplets during emulsification.

Table 7 Visual comparison of oleogels and the effect that changing shear, water concentration, and EC concentration has on emulsion microstructure.

Sample	Emulsion	40x Magnification	100x Magnification
1			
2			
3			
4			

5			
6			
7	 	N/a	N/a

8	 	N/a	N/a

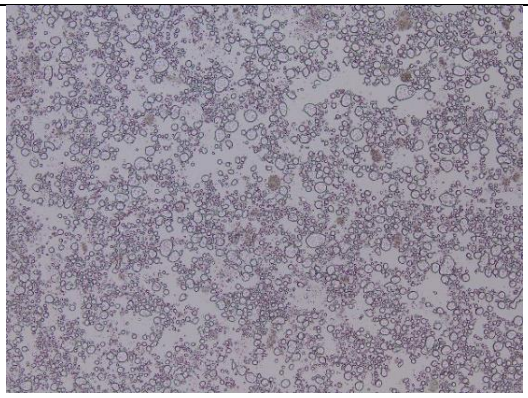
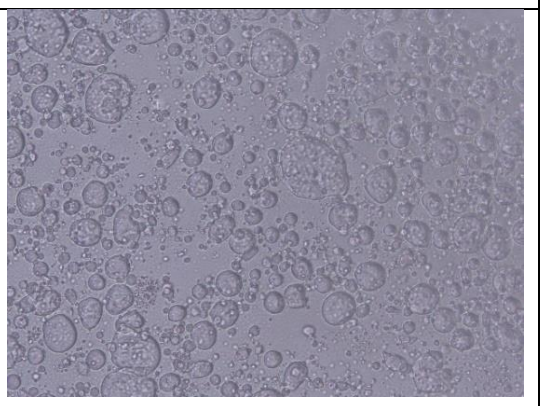
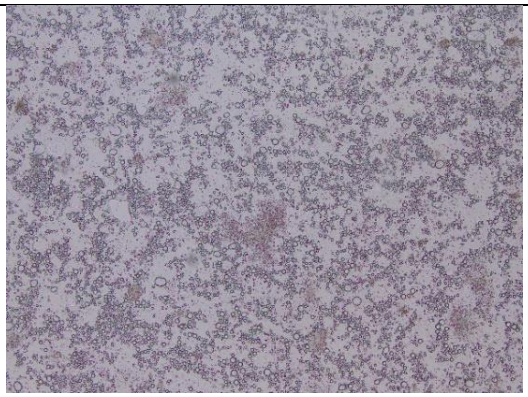
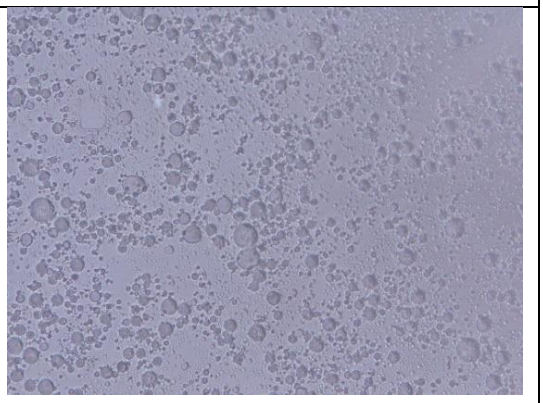
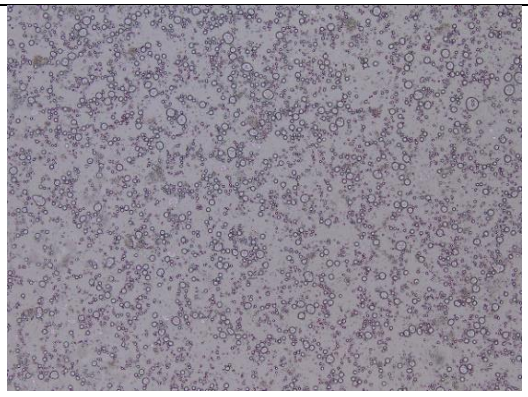
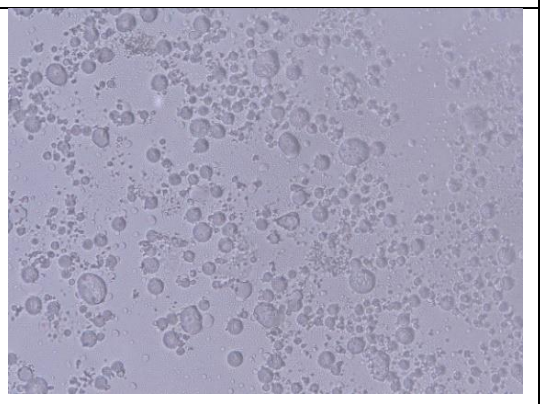
7.2.3 Effect of storage temperature on emulsion stability

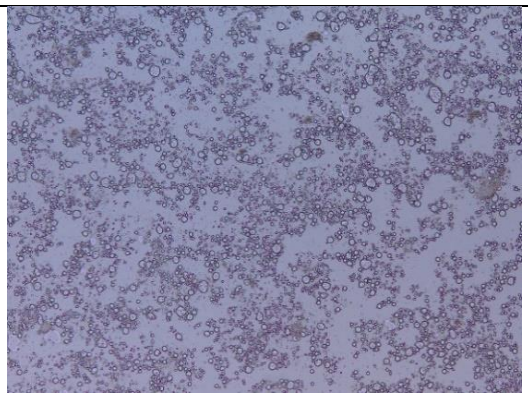
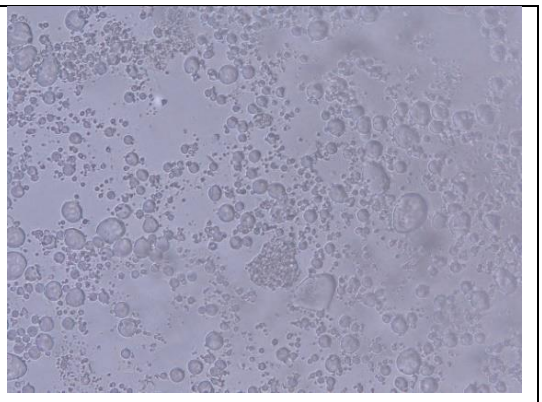
Sample 1 x40 contains large droplets (emulsion parameters described in table 8, droplets pictured in table 9) which demonstrate that the emulsion has poor freeze-thaw stability. There does not appear to be a large difference between the samples at 25°C and 40°C demonstrating some stability at higher temperatures. The emulsion does appear to have the smallest water droplet size at 5°C which was expected as there was no visible oil separation on the sample.

Table 8 Parameters used for assessing the influence of temperature on emulsion stability.

Sample	Water (w/w%)	EC (w/w%)	Shear (rpm)	Storage temp (°C)
1	20	3	20500	-20
2	20	3	20500	5
3	20	3	20500	25
4	20	3	20500	40

Table 9 Visual comparison of the water droplet size at x10 and x40 magnification of emulsion held at different storage temperatures.

Sample	x10	x40
1		
2		
3		

4		

7.2.4 Visual stability test

This test looked at the stabilisation of the EC oleogel-emulsion. Two emulsions were prepared for this analysis, a 3 w/w% EC and a 5 w/w% EC emulsion and both samples contained 20 w/w% water. Images were taken at day 1, 7, and 28 to document any phase separation. These images are shown in figure 10, 11 and 12. No water separation was observed, as this would be visible at the bottom of the glass tubes due to water being denser than oil. Some oil separation is observed after 7 days (0.2 – 0.3 mL), and more is observed after 28 days (~0.5 mL). It is difficult to read exactly how much oil separation has occurred as air bubbles have coalesced and risen to the oil separation layer as well. Some small air bubbles can be observed after day 7, but this is much clearer in the image from day 28. It is assumed that these are air bubbles rather than water droplets, as water droplets would have sunk to the bottom of the tube, again due to the density difference.

Figure 10 Visual stability test images of oleogel emulsions made with 3 w/w% EC (left) or 5 w/w% EC (right) and 20 w/w% water on day 1.

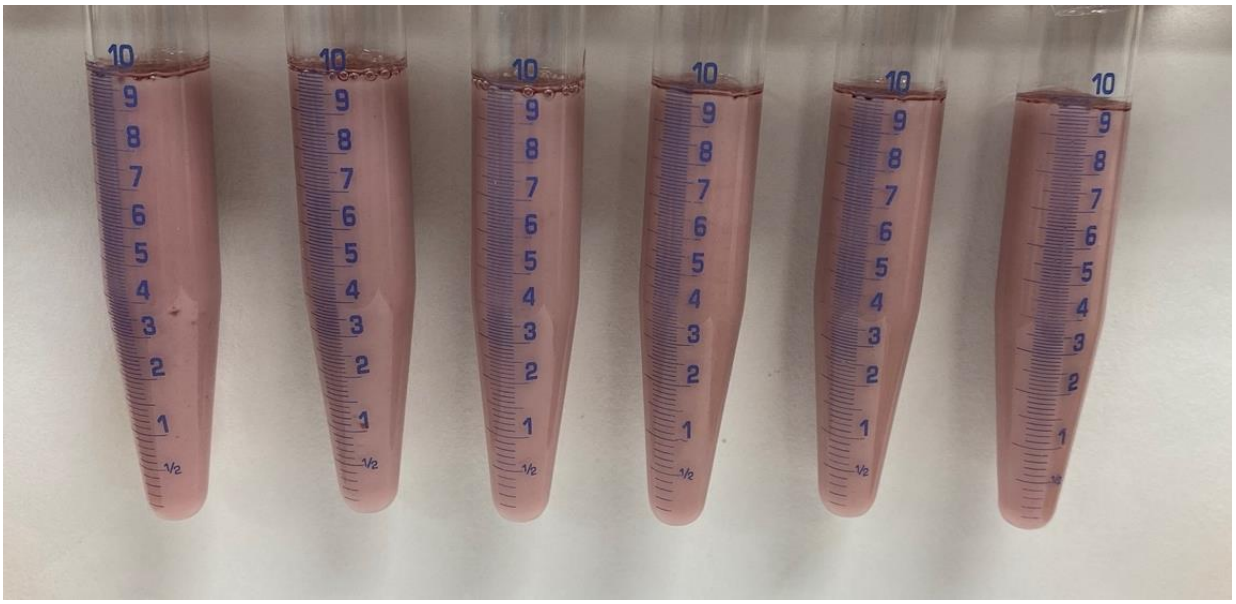


Figure 9 Visual stability test images of oleogel emulsions made with 3 w/w% EC (left) or 5 w/w% EC (right) and 20 w/w% water on day 7.

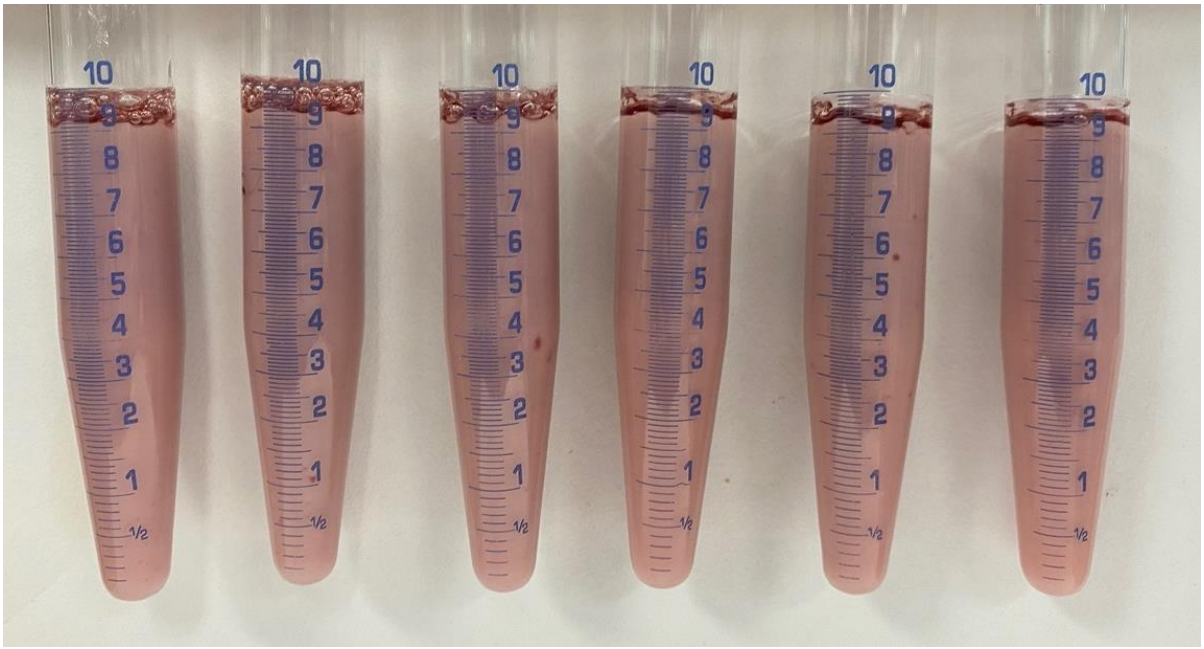


Figure 10 Visual stability test images of oleogel emulsions made with 3 w/w% EC (left) or 5 w/w% EC (right) and 20 w/w% water on day 28.

7.2.5 Strain Sweep

Strain sweep tests were conducted on a oleogel-emulsions made with 20 w/w% water and either 3 w/w% EC or 5 w/w% EC. Multiple samples were prepared, with a sample being tested on day 1 and a second sample being tested on day 7. The results from the 5 w/w% EC sample showed a higher modulus demonstrating that a stronger gel is formed compared to the 3 w/w% EC emulsions. The increase in moduli between day 1 and day 7 is very similar for both concentrations, this increase could be due to the extra time that the day 7 emulsions have for the structure to arrange and stabilise. All samples tested show G'>G" behaviour and moduli decrease indicating that the gel is becoming weaker as strain increases above 1 w/w%. This was also seen in the oleogel strain sweep test as gels also reached a critical strain at 1 w/w%.

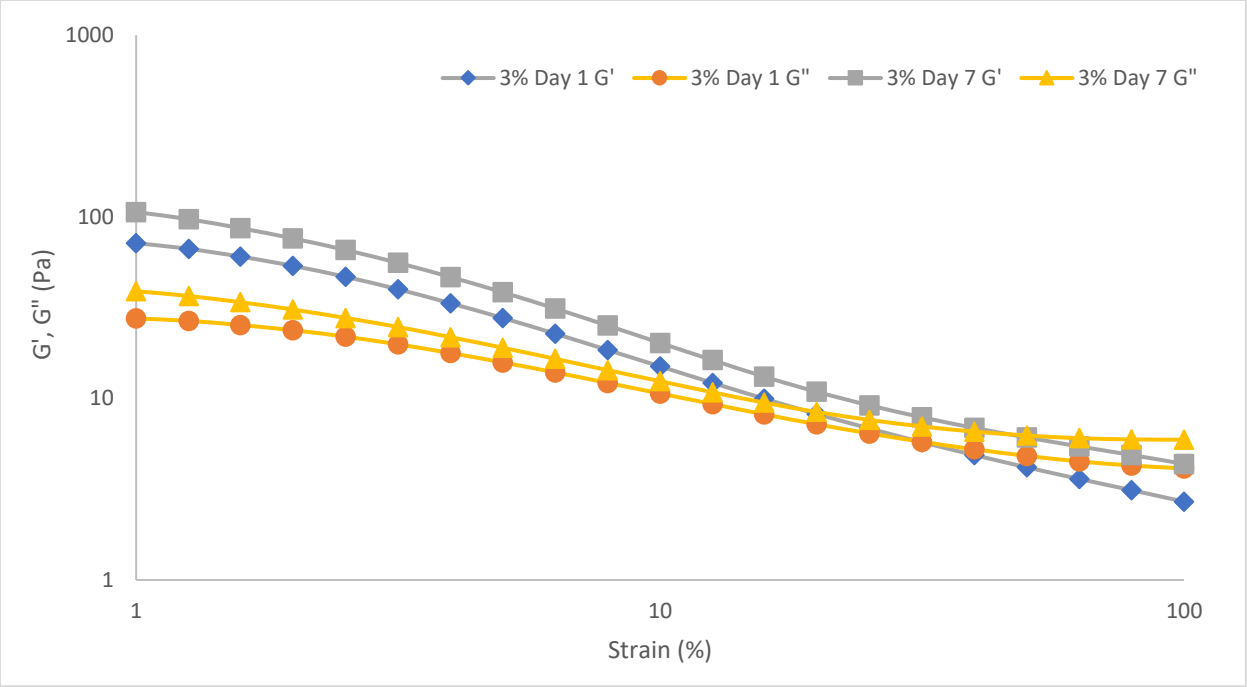


Figure 11 Strain sweep test of 3 w/w% EC, 20 w/w% water oleogel-emulsion samples on day 1 and day 7 at 20°C with frequency fixed at 1 Hz

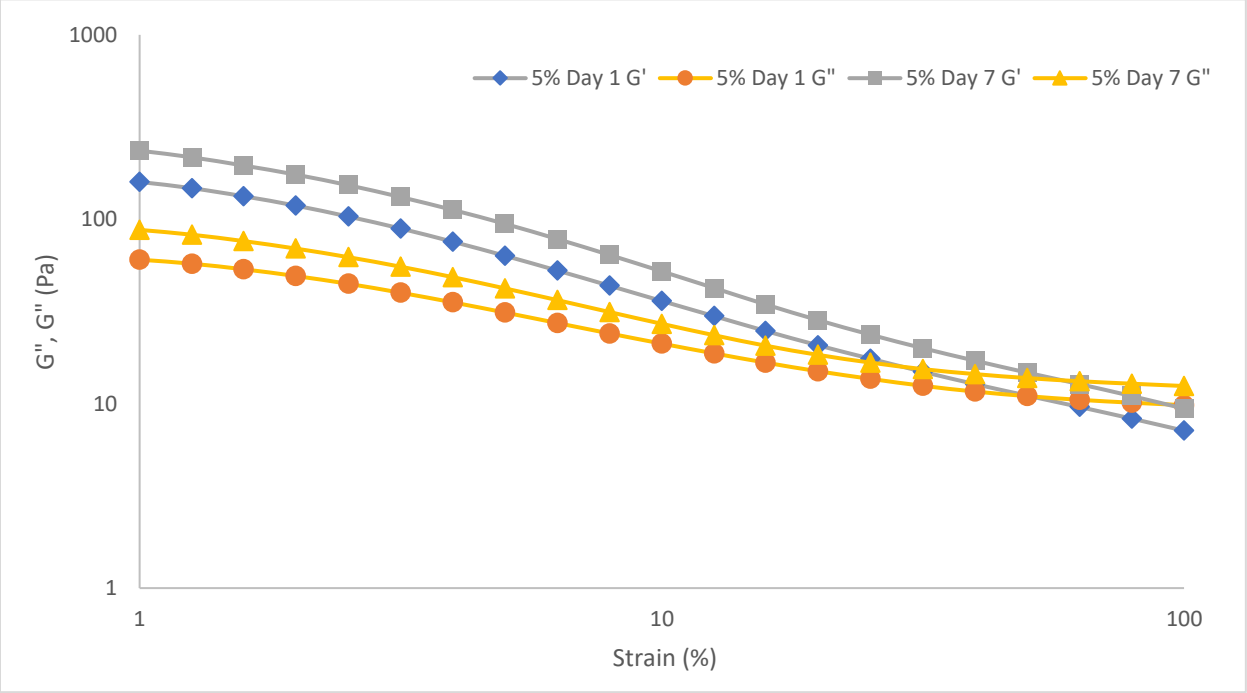


Figure 12 Strain sweep test of 5 w/w% EC, 20 w/w% water oleogel-emulsion samples on day 1 and day 7 at 20°C with frequency fixed at 1Hz

7.3 Discussion

This study confirms that it is possible to stabilise water within an EC oleogel system and maintain gel properties after shear. The amount of time required to form an emulsion was determined by the shear speed and the size of the sample. Larger volumes require more time for sufficient emulsification. The microscopy results demonstrated that a higher shear setting corresponded to a smaller aqueous particle size, however the difference in emulsion stability was minimal. A key observation during microscopy was that the droplets appeared to be covered with particles. It is possible that the shear was breaking up the oleogel and microparticles of EC oleogel were able to stabilise the surface of the droplets during emulsification, this behaviour is seen in Pickering emulsions.

The 3 w/w% oleogel-emulsion could stabilise 50 w/w% water, however the 5 w/w% oleogel-emulsion could not and instead syneresis was observed. This was surprising as it was originally thought that the higher concentration of EC would be able to emulsify more water. This phenomenon is also seen in some starch gels which is caused by the starch gel shrinking and a layer of water forms on top as a result. This is the release of water during retrogradation and is commonly referred to as syneresis. Finding how much water can an EC oleogel-emulsion can stabilise was not exhausted during this study, but this could be worth exploring in future work.

The visual stability test indicated that there was very little difference in stability between the 3w/w% and 5 w/w% EC oleogels. It was promising to see that no water separated from the emulsion. However, an oil layer gradually appeared on the surface of each emulsion. It is suspected that this is the coalescence of oil droplets as they are squeezed out of the system. Bubbles can be seen in the oil layer of the 3 w/w% oleogel-emulsion. It is suspected that these may be air bubbles as they are colourless and the emulsions had dye added to colour the oil and water phases. The bubbles appear to become larger and more obvious with time. The increased viscosity of the gelled oil phase clearly helps with emulsion stability.

Overall, both the 3 w/w% and 5 w/w% oleogel-emulsions performed well at stabilizing 20 w/w% water and there was very little difference between the two systems in terms of emulsion stability. Future work in this space should investigate the application of an EC oleogel emulsion to different W/O templated food applications, such as ice creams, spreads, and bakery margarines.

8.0 General discussion

This study aimed to gain an understanding of oleogels and the critical factors affecting oleogel development. The critical factors involved with developing an oleogel was the temperature require to induce gelation, and the holding time once the solution reached the gel point temperature. To achieve gelation, Gravelle et al. (2018) stated that the oil and EC solution should reach between 125-140°C depending on the viscosity grade (cP) of EC used. However, this study found that reaching 150°C was more effective. Initial trials where samples were heated to 130-140°C showed variation in gel hardness. This could have been due to the equipment, and gelation methods. Many other studies used a convection oven and overhead stirrer, whereas this study used a magnetic hotplate and stir bar. A convection oven would offer less heat loss so it is quite possible that 140°C or lower may be sufficient for gelation. However, the rate of heating would be much slower which could increase the rate of oil oxidation. When the samples were heated to 170°C which approximately the EC melting point, the canola oil oleogel began showing signs of oxidation; a colour change from light yellow to a darker yellow/brown, and smoke. This 'burned' sample formed a very hard gel which agreed with the findings from Gravelle et al. (2012) who commented that a high peroxide value associated with oxidated oil can increase gel hardness.

The next focus was to understand how EC oleogels behave in response to stress. Changes in viscosity due to the application of shear provides important information about a materials processing and performance. The oleogels displayed shear thinning behaviour across both sweep and thixotropy tests which was observed by a decrease in viscosity with increasing shear rate. This is important for food manufacturers if oleogels are going to be used as an ingredient in food applications, as non-Newtonian fluid behaviour can cause issues during processes such as stirring, dispensing, and pumping.

Oleogels are not as solid as typical fats, this could be beneficial in certain food applications. There are ways to increase the hardness of oleogels such as the inclusion of surfactants and using multiple gelators for a synergistic effect. Incorporating an oleogel into the fat phase of a food product as a substitute, or partial substitute, has potential as EC oleogels are heat stable up until 80°C as seen in the temperature sweep test. Applications where this could be useful include spreads and ice creams, particularly for markets with a hot climate such as Asia.

The final area of research explored in this study was looking at the structure and stability of EC oleogel-emulsions. At the beginning of this study, it was not known if forming a gelled emulsion would be possible due to the high gelation temperature. However, it was proved that an EC oleogel can form a stable emulsion with up to 50 w/w% water. Also, the amount of water that the emulsion can stabilise is dependent on the concentration of EC used. While the viscosity may be reduced after shear, the oleogel-emulsions retained a reasonably high viscosity and became opaque – an almost “creamy” texture.

9.0 Conclusions and recommendations

To summarise, this study has successfully demonstrated the potential for oleogels, and oleogel-emulsion to be incorporated into food applications. Saturated fats are becoming increasingly unpopular due to their negative implications on human health when consumed in high amounts. Interest in alternative fat structuring methods has developed because of this, and there is a growing amount of research proving the potential for oleogel technology to fill this gap in the market. Oleogel-emulsions is a novel area of research combining oleogel and biphasic gel technologies, this study has proved the concept is possible using EC as a structuring agent.

There is more to be explored in the space of EC oleogel-emulsions. For research purposes, testing the capacity limits of how much water can be stabilised in and EC oleogel-emulsion system could be of value. The EC and water concentrations tested here were 3 w/w% and 5 w/w% EC with 20 w/w% and 50 w/w% water, however it would be possible to continue decreasing the concentration of EC, which would increase the capacity for how much water can be emulsified.

An area not explored in this study is the incorporation of surfactants or multiple gelators. The benefits this could offer include reducing the total gelator concentration, which both lowers costs and makes it easier to meet FDA regulations for additive limits, which would give the product GRAS status to be produced commercially. This is an area that has been explored with oleogels, but it could be of interest to test with an oleogel-emulsion as well. Another method for increasing stability could be to look at gelling the aqueous phase as well as the lipid phase using starch or gelatin. The application of oleogels into W/O based food such as ice cream, margarine, cream cheese, or spreads is popular in the oleogel research space. Ice creams and bakery margarines are applications that are extremely popular foods yet contain high amounts of saturated fats. The development of a healthier alternative that still retains the characteristic sensory and textural properties that consumers love would be very valuable.

10.0 References

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