

# Green Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

# The replacement for petrolatum: thixotropic ethylcellulose oleogels in triglyceride oils

Terri A. Stortz and Alejandro G. Marangoni\*

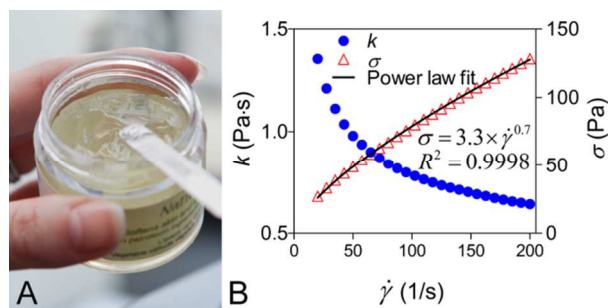
Dept. of Food Science, University of Guelph, 50 Stone Road East, Guelph, ON, N1G 2W1

Canada (Tel.: +1 519 824 4120x5434; fax: +1 519 824 6631; e-mails: [tstortz@uoguelph.ca](mailto:tstortz@uoguelph.ca);

[amarango@uoguelph.ca](mailto:amarango@uoguelph.ca))

## Table of contents entry

Ethylcellulose oleogels were engineered to be thixotropic such that they recover their viscosity after shearing which allows them to be more easily manufactured into food and cosmetic products.



## Abstract

An ethylcellulose (EC) organogel was engineered with thixotropic properties in order to replace petrolatum, the petroleum jelly used extensively as a structuring agent in cosmetics, and the main component of Vaseline<sup>TM</sup>. EC has been used to form oleogels with vegetable oils as the solvent phase. These gels tend to set at very high temperatures and, once set, can be irreversible broken

by shear forces such as those present during manufacture and use. To overcome this, thixotropic EC oleogels were produced that can recover all of their viscosity after removal of the shear. By changing the solubility parameters of the oil phase, particularly by matching the Hansen hydrogen bonding solubility parameter of the oil phase to that of EC, such as by addition of glycerol monooleate, the solubility of the EC in the oil can be increased. This increase in solubility leads to the production of fully thixotropic gels with viscosities that can be tailored by altering the EC concentration or viscosity. Furthermore, a gel made with 5-8% EC 10 cP and 40-50% glycerol monooleate in a variety of oils has favourable texture and water vapour barrier properties which make it a good candidate for use in cosmetics as a replacement for petroleum jelly.

## 1 Introduction

Petrolatum is derived from petroleum and has been identified as a potentially carcinogenic cosmetic ingredient.<sup>1</sup> Its carcinogenicity is caused by contamination with polycyclic aromatic compounds.<sup>2</sup> Full refining of the petrolatum has the potential to remove the carcinogenic compounds<sup>3</sup> however, if the full refining history is unknown then petrolatum is classified as carcinogenic in Europe.<sup>1</sup> The potential negative effects of petrolatum on human health and the desire to use ingredients made from sustainable and renewable resources has prompted a search for potential replacements. Due to the ubiquitous use of this material in personal care products, it is important to find green, commercially and technologically viable replacements.

Organogels have shown great promise for use in the cosmetic industry for their desirable properties such as offering structuring while maintaining product glossiness<sup>4</sup>, ease of

manufacture, and long term stability.<sup>5</sup> Ethylcellulose (EC) has been identified as a polymer organogelator.<sup>6-8</sup> It is also used as a binder, thickener, stabilizer and film former in some cosmetic products such as nail polish, lipstick or fragrances.<sup>9</sup> EC organogels have also been studied as fat replacers.<sup>10</sup> An organogel with a fatty acid profile very high in unsaturated fatty acids, low in saturated fatty acids, and having zero *trans*-fatty acids could be used to replace fats typically high in saturated and *trans*-fatty acids which could offer health benefits.<sup>11</sup> Organogels are advantageous compared to liquid oils because they offer functional benefits such as reduced oil migration<sup>12</sup> and texture profiles which more closely match solid fats.<sup>10</sup>

It has been observed that the addition of surfactants to the EC organogel system can result in marked changes in the properties of the organogel including altering the appearance, mechanical strength<sup>13</sup>, and gelation and melting temperatures<sup>14</sup> among other things.<sup>15</sup> It is thought that the surfactant has the ability to plasticize the EC<sup>8</sup> and the properties of the surfactant such as the headgroup size would allow different degrees of plasticization.<sup>16</sup> Therefore, the viscosity of EC oleogels with various surfactants over a large range of concentrations will be studied with the aim of producing a thixotropic oleogel.

Thixotropy is a rheological term that describes a material that thins with time at a fixed shear rate and exhibits an increase in viscosity upon removal of the shear force.<sup>17</sup> EC gels tend to set at

very high temperatures and when subjected to shear after setting the gel irreversibly breaks causing loss of its functionality. This makes it difficult to add EC gels to some products. However, if the gel were thixotropic then processes which require shear after the gel sets would not be as problematic since the gel would be able to recovery its viscosity and functionality over time once the shear was removed. Furthermore, petroleum jelly is thixotropic<sup>18</sup> therefore this property would be highly desirable in a replacement product.

## 2 Materials and Methods

### 2.1 Gel preparation

ETHOCEL<sup>TM</sup> standard ethoxy content, premium grade EC polymers with viscosity of 10, 20 or 45 cP were obtained from Dow Chemical Company. Various oils and surfactants were used to make the samples; these ingredients are listed along with their sources and abbreviations used throughout the text. The EC powder was mixed with the oil and/or a surfactant. Formulas are described by the concentration of EC in wt% and the ratio of surfactant to oil in the fat phase. For example a formula may be made with 8% EC 10 cP and 40:60 glycerol monooleate:HOSO. The ingredients were heated to 100-140°C on a hotplate with a stir bar to dissolve the EC. Once fully dissolved the mixture was aliquoted into three glass vials with 10 g of sample and left to set at room temperature.

**Table 1** Ingredients used and their abbreviations and sources

Ingredient	Abbreviation	Source
Ethylcellulose	EC	Dow Chemical Company, Midland, MI
High oleic sunflower oil	HOSO	Nealanders International Inc., Mississauga, ON
Canola oil	-	ACH Food Companies, Inc., Mississauga, ON
Soybean oil	Soy	Loblaws, Toronto, ON
Flaxseed oil	Flax	Omega Nutrition Canada Inc., Vancouver, BC
Avocado oil	-	Metro Inc., Montréal, QC
High oleic canola oil	HOCO	Nealanders International Inc., Mississauga, ON
High stearic sunflower oil	HSSO	Advanta Ltd., Mar del Plata, Argentina
Medium chain triglyceride oil	MCT	Stepan Company, Northfield, NJ
Neobee <sup>®</sup> 1053		
Glycerol monooleate		HallStar Company, Chicago, IL
Sorbitan monooleate		Sigma Aldrich, Steinheim, Germany
Triglycerol monooleate		Stepan Company, Northfield, NJ
Drewpol <sup>®</sup> 3-1-O		
Decaglycerol decaoleate		Lonza Group Ltd., Allendale, NJ
Polyaldo <sup>®</sup> DGDO		

## 2.2 Viscosity measurement

The viscosities of the gels were measured using an AR 2000 rheometer (TA Instruments, New Castle, DE). After 2 days of storage the samples were sheared by hand in their vials for 15 rotations clockwise and 15 rotations counter clockwise using a flat spatula to assist with transfer onto the base plate of a rheometer. A 60 mm 2° acrylic cone was lowered into the sample to a

gap size of 900  $\mu\text{m}$  and the temperature was set to equilibrate to 25°C. A steady state flow test with the shear rate ramping from 20-200  $\text{s}^{-1}$  was used to measure the initial viscosity of the sample. This was followed immediately by a ramp from 200-20  $\text{s}^{-1}$  to give a measure of the immediate viscosity recovery. The sample was then removed from the base plate and placed in a glass vial for storage. The viscosity recovery after one week of storage was tested on the same sample using a ramp from 20-200  $\text{s}^{-1}$ . Three replicates were measured for each sample.

The power law model<sup>17</sup>, given in **Equation 1**, was fitted to the data of a viscosity versus shear rate flow curve.

$$\sigma = k \times \dot{\gamma}^n \quad (1)$$

The power law model has that the shear stress ( $\sigma$ ) is equal to a consistency coefficient ( $k$ ), times the shear rate ( $\dot{\gamma}$ ) to the power of  $n$  where  $n$  is the power law index and indicates the type of flow observed. For Newtonian behaviour  $n = 1$ ; for shear thinning (pseudoplastic)  $n < 1$ ; and for shear thickening fluids  $n > 1$ . The value of  $k$  will be used throughout our analyses as an indicator of viscosity.

### 2.3 Oil density measurement

A DE40 density meter (Mettler Toledo, Mississauga, ON) was used to measure the density of the oils and surfactants used in the various formulas. The samples and deionized water were equilibrated to 25°C. The water was used first to perform the daily check. Samples were then tested. The density meter measures density by comparing the resonance frequency of the glass U-tube when filled with air versus water versus the sample during electromagnetic induction. Since air and water have known densities the density of the sample can be calculated from the period of oscillation of vibration when the U-tube is filled with the sample.

## 2.4 Hansen solubility parameter calculations

Hansen solubility parameters (HSPs) are made up of dispersion forces ( $\delta_d$ ), polarity ( $\delta_p$ ), and hydrogen bonding ( $\delta_h$ ) according to **Equation 2**:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2)$$

The HSPs for each oil and glycerol monooleate mixture were calculated using literature values. The HSPs of HOSO was not available; however, most vegetable oils have similar HSPs therefore the HSPs for sunflower oil were used as close approximations. The densities of the glycerol monooleate and HOSO were measured and used to convert the wt% of each component into volume percent since energies of vaporization are calculated on a volumetric basis. The dispersion parameters for the surfactant (surf) and oil were then multiplied by their respective volume fraction in the system ( $\Phi$ ) and summed to give the  $\delta_d$  for the mixture at each glycerol monooleate concentration (**Equation 3**).

$$\delta_d \text{ mix} = (\Phi_{surf} \times \delta_d \text{ surf}) + (\Phi_{oil} \times \delta_d \text{ oil}) \quad (3)$$

This was repeated for the  $\delta_p$  and  $\delta_h$ . The total  $\delta$  for the mixture was then calculated using **Equation 2**. The HSPs for the mixtures were then compared to the literature values for HSPs of ethylcellulose since materials with similar HSPs will be more likely to dissolve into one another.<sup>19</sup>

## 2.5 Water vapour transmission rate

A gel formula with good viscosity, texture, and full thixotropy was tested for its water vapour permeability using a method similar to that described by Martini et al.<sup>20</sup> A mixture of 3% hydroxypropyl methyl cellulose (The Dow Chemical Co., MI, E15), 37.5% w/w of silica gel (Fisher Scientific, NY, grade 60, 230-400 mesh), 13.2% of a saturated solution of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , and 46.3% deionized water was prepared. This mixture was measured as having a relative



humidity (RH) at 20°C of 96% and was used as the water source for the experiment. AQUALAB plastic sample cups (Decagon Devices, Inc., WA) were used as sample holders and were filled with 12 g of the silica gel mixture leaving approximately 2 mm of height to the top of the cup. The cups were then placed in a freezer at -20°C and left to freeze to ease the spread of sample on top of the silica gel. A gel sample was prepared with 8% EC 10 cP and glycerol monooleate and HOSO or avocado oil a ratio of 40:60. Control samples were also prepared with HOSO, avocado oil or petroleum jelly (Vaseline Original Petroleum Jelly, Unilever Canada Inc., Toronto, ON). Samples were stirred with a metal spatula for 15 rotations clockwise and 15 rotations counter clockwise and then spread onto the silica filled cups to fill the remaining part of the cup. The weight of sample added was measured to ensure it was kept relatively constant at 1.6 g. Three replicates were prepared for each sample including an uncovered sample containing only the silica gel. The samples were placed in a sealed desiccator with a saturated solution of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in the bottom to control the humidity at 32.9%. The desiccator was placed in an incubator at 20°C and the weight change of the samples was measured over time. The water vapour transmission rate (WVTR) was calculated using the following equation:

$$WVTR = \text{slope} / A \quad (4)$$

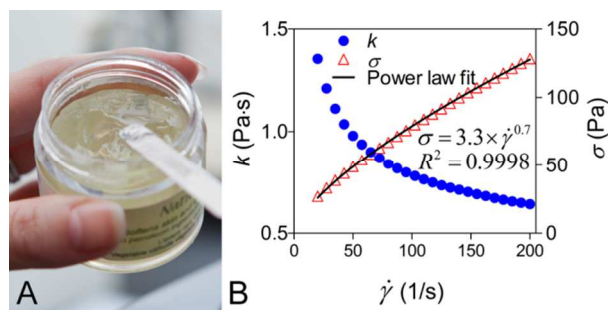
where *slope* is the slope of the linear portion of the weight loss over time (g/days) plot and *A* is the area of the sample which was 12.57 cm<sup>2</sup>.

### 3 Results and Discussion

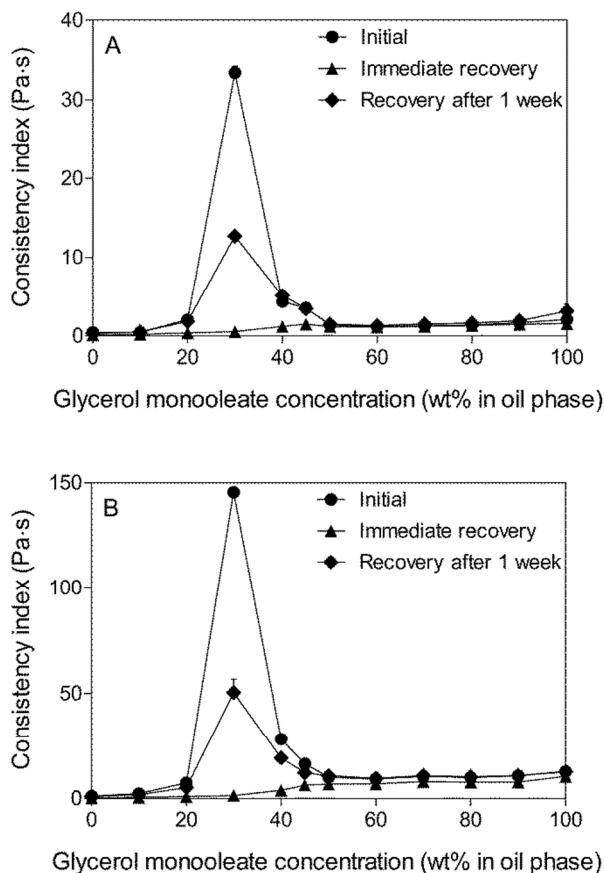
#### 3.1 Effect of glycerol monooleate concentration

The effect of addition of large amounts of surfactant on viscosity of the gels was studied. A typical flow curve result is shown in **Figure 1**. The sample was made with 5% EC 10 cP and

glycerol monooleate:HOSO 45:55. The power law model showed an excellent fit to the shear stress data with an  $R^2 = 0.9998$  and gave a value of  $n = 0.6927$  indicating shear thinning behaviour. All of the samples tested displayed shear thinning. The value for  $k$ , the consistency coefficient, was obtained from the power law fit and plotted against the concentration of glycerol monooleate in the samples (**Figure 2**). Gels were prepared with 5 or 8% EC 10 cP, HOSO, and glycerol monooleate at increasing proportions of the oil phase. Samples made with 8% EC had greater viscosity than those made with 5% EC. The maximum viscosity was achieved at 30% glycerol monooleate at both concentrations of EC; however, this sample displayed only partial thixotropy and showed signs of gel breakage and oil leakage. Gels made with 0-20% glycerol monooleate appeared to be broken during the pre-shear procedure and had very low viscosity, mainly due to the shear-induced structural breakdown. The greatest viscosity and recovery was achieved between glycerol monooleate concentrations of 40-50%. The samples made with 40-45% glycerol monooleate were thus considered as the most promising due to their high viscosity and fully thixotropic character. Subsequent samples were therefore made using these glycerol monooleate:oil ratios. The samples with 4-45% glycerol monooleate also had good texture and low oiliness when spread on the skin which is an important attribute for a cosmetic paste.



**Figure 1** Appearance (A) and viscosity and shear stress with power law fit (B) of a sample made with 5% EC 10 cP glycerol monooleate:HOSO 45:55 (w/w).



**Figure 2** Effect of surfactant concentration on viscosity of gels made with 5% (A) or 8% (B) EC 10 cP, HOSO and glycerol monooleate.

Hansen solubility parameters were used to study if the glycerol monooleate was altering the solubilisation of the EC polymer in the oil phase. HSPs for the gel components and oil-glycerol monooleate mixtures are listed in **Table 2**. All three components have similar values for  $\delta_d$ . The  $\delta_p$  of EC is just slightly higher than that of glycerol monooleate, but much higher than the oil. Therefore, any combination of glycerol monooleate and oil will not give a  $\delta_p$  that matches that of EC. The greater the glycerol monooleate:oil ratio, the closer its  $\delta_p$  value will be to that of EC. Interestingly, the  $\delta_h$  of EC lies in-between that of glycerol monooleate and oil. Therefore, a particular mixture of glycerol monooleate and oil will have a  $\delta_h$  that matches that of EC which is around  $9.70 \text{ MPa}^{0.5}$ . It is clear from the calculated values of HSPs for glycerol monooleate

mixtures that as the concentration of glycerol monooleate is increased, the  $\delta_h$  increases until it reaches  $9.65 \text{ MPa}^{0.5}$  at a mixture of 45 wt% glycerol monooleate and 55 wt% oil. This particular combination of glycerol monooleate and oil gave a superior product with almost full thixotropy, high viscosity, and good texture when applied to the skin. It is thought that at this glycerol monooleate:oil ratio, the EC has achieved near ideal solubility in the system. As the glycerol monooleate:oil ratio is increased to 60-70% the total solubility parameter ( $\delta$ ) of the system reaches that of EC. At high glycerol monooleate ratios, therefore, there were no marked differences between the gels. We can conclude that hydrogen bonding, and therefore  $\delta_h$ , in the system plays the major role in determining the gel's rheological behaviour. Below 45% glycerol monooleate the EC achieved only partial solubility. Within the range of 20-45% glycerol monooleate the EC was ideally solubilised for gelation to occur. Partial solubility of the gelator in the solvent is necessary for gelation.<sup>21</sup> This is why a peak in gel viscosity was observed at 30% glycerol monooleate. At concentrations less than 20% glycerol monooleate gels were still formed, however, they were much weaker and the EC was not solubilised enough to produce a thixotropic gel. Thus, the physical properties of EC oleogels display two distinct types of behavior depending on which side of the maximal viscosity-solubility parameter critical region they occupy. In the low surfactant range we encounter solid-gel type behavior, with limited thixotropy, while in the high surfactant range the gels behave more like pastes, with strong thixotropic character.

### 3.2 Effect of EC concentration

The effect of EC concentration is shown in **Figure 3**. As the concentration of EC increased the viscosity of the gel also increased. This was expected since the greater the amount of polymer in the system, the more polymer-polymer junction zones can be formed creating a stronger gel

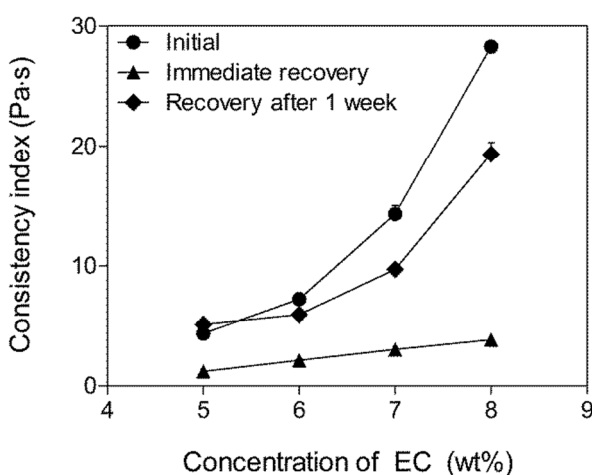
network. It was also observed that the proportion of the viscosity that was recovered after one week of storage was close to 100% for concentrations of 5 and 6% but decreased to around 70% for concentrations of 7 and 8% EC. The solvent HSPs would be the same at all of the EC concentrations; therefore, differences in the proportion of recovered viscosity are slightly perplexing. Perhaps, it is related to gelation behaviour rather than solution behaviour. The higher viscosity of the 7 and 8% EC gels may limit the ability of the swollen polymers to diffuse within the solvent and find neighbouring polymers with which to interact. This would limit the gels' ability to reform all of the tie points that were present in the initial sample resulting in the lower viscosity of the gel after one week of recovery.

**Table 2 Literature and calculated HSPs (in MPa<sup>0.5</sup>) for gel components and combinations thereof**

Literature values	$\delta_d$	$\delta_p$	$\delta_h$	$\delta$
<b>EC 10 cP<sup>22</sup></b>	16.60	8.30	<b>9.70</b>	20.90
Sunflower oil <sup>23</sup>	16.00	1.50	4.70	16.70
Glycerol monooleate <sup>24</sup>	16.10	7.50	15.90	23.80
Calculated values for oil and glycerol monooleate mixtures				
10% glycerol monooleate*	16.01	2.08	5.79	17.15
20% glycerol monooleate	16.02	2.67	6.88	17.64
30% glycerol monooleate	16.03	3.26	7.98	18.20
40% glycerol monooleate	16.04	3.85	9.09	18.83
<b>45% glycerol monooleate</b>	16.04	4.15	<b>9.65</b>	19.17

50% glycerol monooleate	16.05	4.45	10.20	19.53
60% glycerol monooleate	16.06	5.05	11.33	20.29
70% glycerol monooleate	16.07	5.66	12.46	21.11
80% glycerol monooleate	16.08	6.27	13.60	21.97
90% glycerol monooleate	16.09	6.88	14.75	22.88

\* wt% of glycerol monooleate in a mixture of glycerol monooleate and HOSO

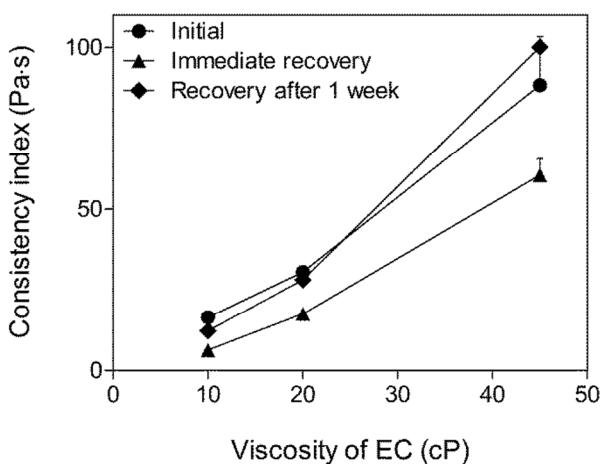


**Figure 3** Effect of EC concentration on viscosity of gels made with EC 10 cP and glycerol monooleate:HOSO at 40:60 (w/w).

### 3.3 Effect of EC molecular weight

The effect of EC molecular weight (expressed as a viscosity in cP) on the viscosity and recovery of the gels is shown in **Figure 4**. There was a clear trend of increasing gel viscosity with increased EC viscosity. This trend was expected since the higher molecular weight EC polymers would swell to a greater size and lead to a greater viscosity in the gel. All of the EC viscosities showed nearly 100% viscosity recovery after one week of storage. The HSPs of EC is very similar at the different viscosities.<sup>22</sup> Therefore, it was expected that these gels show similar behaviour. The gel made with EC 45 cP had a very high viscosity and therefore its texture was

very thick which was thought to be less desirable in a cosmetic paste than those gels made with 10 or 20 cP.



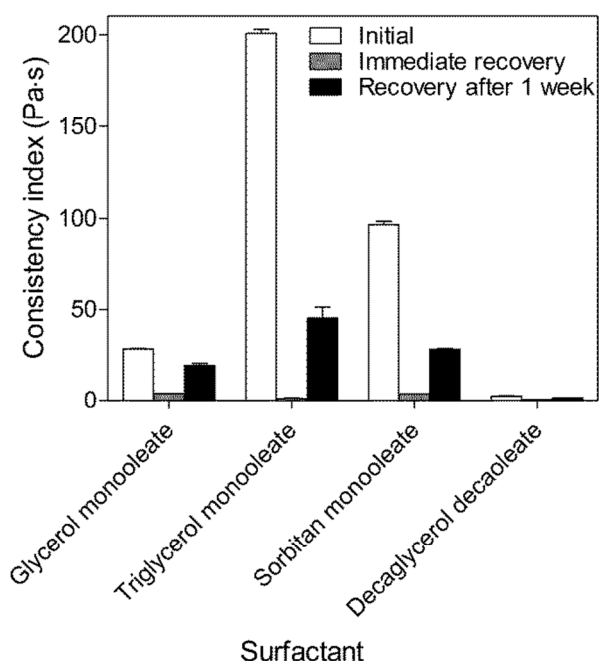
**Figure 4** Effect of EC viscosity on the viscosity of gels made with 8% EC and glycerol monooleate:HOSO at 45:55 (w/w).

### 3.4 Effect of surfactant type

The results have clearly shown that addition of large amounts of glycerol monooleate to an EC oleogel led to the development of a thixotropic gel. Several other surfactants were studied for their efficacy in producing thixotropic gels. Sorbitan monooleate, triglycerol monooleate, and decaglycerol decaoleate are common food grade surfactants that were mixed with HOSO and EC to produce gels (**Figure 5**). Triglycerol monooleate and sorbitan monooleate both showed much higher initial viscosity than glycerol monooleate but they recovered only less than 30% of their viscosity after one week. It is thought that these surfactants aren't as good solvents for EC as glycerol monooleate. It is likely that the differences observed are due to differences in the Hansen solubility parameters for the various surfactants. Sorbitan monooleate has a lower  $\delta_h$  than glycerol monooleate (**Table 3**) at  $10.3 \text{ MPa}^{0.5}$  compared to  $15.9 \text{ MPa}^{0.5}$ . The solubility parameters for the sorbitan monooleate-oil mixture were calculated using the volume fraction

method in **Equation 3** for the oil phase of the 40:60 sorbitan monooleate:HOSO sample and the experimentally determined density which was 0.9893 g/mL. The  $\delta_h$  for the sorbitan monooleate mixture was much lower than that of the glycerol monooleate mixture. Therefore, the EC was better solubilized in the sample made with glycerol monooleate leading to the greater proportion of viscosity recovery. The EC was less solubilized in the sorbitan monooleate sample which led to better gelation of the EC in this sample and the corresponding high viscosity with low viscosity recovery. This is similar to what was observed in the peak region in **Figure 2**. Unfortunately, solubility parameters were not available for triglycerol monooleate or decaglycerol decaoleate. It would be expected that triglycerol monooleate would have an even lower hydrogen bonding parameter than sorbitan monooleate, and decaglycerol decaoleate would have the lowest of them all. Therefore, EC would have the poorest solubility in decaglycerol decaoleate at this surfactant concentration. Adding a greater amount of these surfactants might change the solubility of EC in the oil phase leading to a thixotropic gel. However, that is not ideal since the surfactants would likely have a greater cost than the oil.





**Figure 5** Effect of surfactant type on viscosity and recovery of gels made with 8% EC 10 cP and a surfactant:HOSO ratio of 40:60 (w/w).

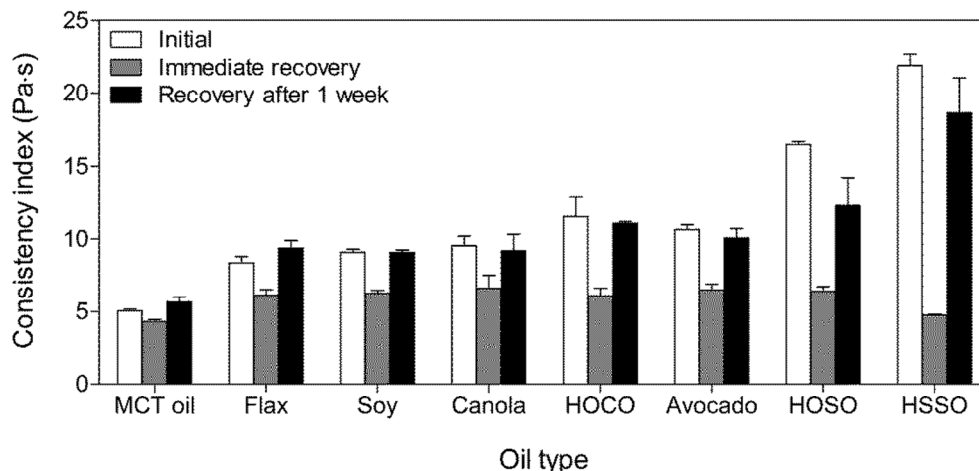
**Table 3** HSPs for sorbitan monooleate and its mixture of 40% in oil

Literature values	$\delta_d$	$\delta_p$	$\delta_h$	$\delta$
EC 10 cP	16.60	8.30	9.70	20.90
Sorbitan monooleate <sup>25</sup>	17.20	7.70	10.30	21.48
Calculated values for oil and surfactant mixtures				
40% glycerol monooleate	16.04	3.85	9.09	18.83
40% sorbitan monooleate	16.46	3.86	6.83	18.23

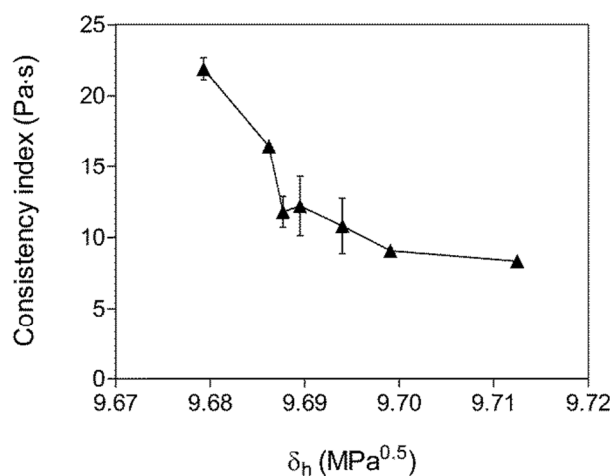
### 3.5 Effect of oil type

Several different types of oils were tested for their efficacy in creating thixotropic gels. Medium chain triglyceride (MCT) oil is widely used as cosmetic oil and is made using coconut or palm

kernel oils. All of the oils tested showed similar results with only small variations in viscosities and all oils were able to create a thixotropic paste (**Figure 6**). The gel made with MCT oil showed a lower viscosity and an immediate recovery viscosity that was very close to its initial and recovered viscosities. This oil<sup>26</sup> has  $\delta_h = 4.1 \text{ MPa}^{0.5}$  whereas that of the other oils is around 4.6-4.7  $\text{MPa}^{0.5}$ .<sup>23</sup> However, not all of the oils tested have been characterised for HSPs, so further comparisons cannot be made. The small variations in viscosity observed can also be explained by variations in the densities of the oils tested. HSPs are calculated based on volume fractions however these samples were made based on equal weight proportions of glycerol monooleate to oil. Therefore, samples with oils of higher density would end up having a slightly lower volume fraction of oil to glycerol monooleate and therefore a higher  $\delta_h$  than oils of lower density since more glycerol monooleate results in a greater  $\delta_h$ . The  $\delta_h$  for each of the oil mixtures except MCT oil was estimated using the measured densities of the oil and  $\delta_h = 4.7 \text{ MPa}^{0.5}$ . A plot of initial gel viscosity versus  $\delta_h$  (**Figure 7**) shows the expected trend that as the  $\delta_h$  approaches that of EC (9.70  $\text{MPa}^{0.5}$ ) the viscosity decreases indicating a loss of EC gelation due to greater solubilisation of the EC. This mimics the right-hand side of the peak observed in **Figure 2** depicting the viscosity of the gels with increasing glycerol monooleate concentration.



**Figure 6** Effect of oil type on viscosity and recovery of gels made with 8% EC 10 cP and a glycerol monooleate:oil ratio of 45:55 (w/w).



**Figure 7** Effect of oil phase  $\delta_h$  on the viscosity of gels made with 8% EC 10 cP and a glycerol monooleate:oil ratio of 45:55 (w/w).

### 3.6 Comparison to a commercial cosmetic product

#### 3.6.1 Water vapour transmission rate (WVTR)

The WVTR of two gels were compared to a commercially available petroleum jelly product. It was found that gels made with 8% EC 10 cP and 40:60 glycerol monooleate:oil significantly reduced water vapour transmission compared to an uncovered control. This was the case for gels

made with HOSO or avocado oil. Interestingly, the ungelled oil offered the same WVTR as the gelled sample. The gelled sample, however, had the added benefit of high viscosity and a reduced oily feeling on the skin compared to the ungelled sample. The commercial petroleum jelly product almost completely blocked the loss of water. Its WVTR was significantly less than those of the gels. Therefore, the gels have good barrier properties, though petroleum jelly did perform better under these test conditions. It is important to note that petroleum jelly has a melting point near body temperature ( $37^{\circ}\text{C}$ )<sup>27</sup> and this would likely affect its barrier properties when used on the skin.

**Table 4 WVTR of gel samples and a comparable commercial product\***

Sample	WVTR $\text{g}\cdot\text{days}^{-1}\cdot\text{cm}^{-2}$ ( $\times 10^{-3}$ )
Uncovered	$49 \pm 11^{\text{a}}$
HOSO	$2.7 \pm 1.5^{\text{b}}$
HOSO gel	$2.8 \pm 0.9^{\text{b}}$
Avocado oil	$3.8 \pm 2.7^{\text{b}}$
Avocado gel	$3.5 \pm 2.0^{\text{b}}$
Petroleum jelly	$0.035 \pm 0.0086^{\text{c}}$

\*Values with the same superscript are not significantly different ( $P < 0.05$ ).

### 3.6.2 Viscosity

The viscosity of a fully thixotropic EC gel can be tailored by modifying the concentration or viscosity of the EC. A formula with 5-8% EC, EC 10-45 cP, 45:55 glycerol monooleate:HOSO can have an initial viscosity ranging from 3.4-99.4 Pa·s. Adjusting the EC concentration beyond the 5-8% interval would likely increase this viscosity range even further. The commercial

petroleum jelly had initial, immediate, and recovered viscosities of  $200.4 \pm 4.9$ ,  $15.1 \pm 2.9$ , and  $168 \pm 37$  Pa·s at 25°C. This product clearly had greater viscosity than any of the EC gel formulas tested and also showed full thixotropy. Again, the melting temperature of petroleum jelly being close to body temperature would greatly change (lower) its viscosity when spread on the skin. This would not occur with the EC gels.

#### 4 Conclusions

The thixotropy of EC oleogels was successfully engineered by modulation of polymer solubility in triglyceride oils. A gel can achieve 0-100% viscosity recovery after shearing depending on how closely the hydrogen bonding solubility parameter of the solvent phase matches that of the EC polymer. Full viscosity recovery was achieved with glycerol monooleate at concentrations of 40-50%. Gels showing full viscosity recovery show great potential for use in food and cosmetic products especially in those products that would introduce shear at temperatures where the gel has already set. Gels have been developed which have favourable textural and water vapour barrier properties for use on the skin.

#### 5 References

- 1 The European Cosmetic Toiletry and Perfumery Association, *Joint COLIPA/ECF recommendation: safety of petrolatum as raw material for cosmetic industry*, 2004.
- 2 D. Mellowship, *Toxic Beauty*, Gaia, London, England, 2009.

- 3 U.S. Environmental Protection Agency, *Hazard characterization document: screening-level hazard characterization; waxes and related materials category, subcategory I: slack waxes*, 2011.
- 4 V. Ferrari, *World Pat. App.*, 02/055030 A2, 2002.
- 5 R. Balasubramanian, A. A. Sughir and G. Damodar, *Asian J. Pharm.*, 2012, **6**, 1-9.
- 6 J. M. Aiache, P. Gauthier and S. Aiache, *Int. J. Cosmetic Sci.*, 1992, **14**, 228-234.
- 7 P. Gauthier, S. Aiache and J. M. Aiache, *Int. J. Cosmetic Sci.*, 1996, **18**, 229-235.
- 8 T. Dey, D. A. Kim and A. G. Marangoni, in *Edible Oleogels: Structure and Health Implications*, ed. A. G. Marangoni and N. Garti, AOCS Press, Urbana, Illinois, 2011, pp. 295-311.
- 9 Dow Cellulosics, *Ethocel ethylcellulose polymers technical handbook*, 2005.
- 10 A. K. Zetzl, A. G. Marangoni and S. Barbut, *Food Funct.*, 2012, **3**, 327.
- 11 R. P. Mensink, P. L. Zock, A. D. M. Kester and M. B. Katan, *Am. J. Clin. Nutr.*, 2003, **77**, 1146.
- 12 N. E. Hughes, A. G. Marangoni, A. J. Wright, M. A. Rogers and J. W. E. Rush, *Trends Food Sci. Technol.*, 2009, **20**, 470-480.
- 13 A. J. Gravelle, S. Barbut and A. G. Marangoni, *Food Res. Int.*, 2012, **48**, 578-583.
- 14 A. G. Marangoni, *World Pat. App.*, 2010/143066 A1, 2010.

- 15 A. J. Gravelle, S. Barbut and A. G. Marangoni, *Food Funct.*, 2013, **4**, 153.
- 16 E. D. Co and A. G. Marangoni, *J. Am. Oil Chem. Soc.*, 2012, **89**, 749-780.
- 17 C. R. Daubert and E. A. Foegeding, in *Food analysis*, ed. S. S. Nielsen, Springer, New York, NY, 2010, pp. 542.
- 18 A. de Waele, *Nature*, 1949, **163**, 248.
- 19 C. M. Hansen, *Hansen solubility parameters: a user's handbook*, CRC Press/Taylor & Francis, Boca Raton, FL, 2007.
- 20 S. Martini, D. A. Kim, M. Ollivon and A. G. Marangoni, *J. Agric. Food Chem.*, 2006, **54**, 1880-1886.
- 21 A. G. Marangoni and N. Garti, in *Edible Oleogels: Structure and Health Implications*, ed. A. G. Marangoni and N. Garti, AOCS Press, Urbana, IL, 2011, pp. 1-18.
- 22 W. L. Archer, *Hansen solubility parameters for selected cellulose ether derivatives and their use in the pharmaceutical industry*, Marcel Dekker, Inc., New York, NY, 2002.
- 23 F. Cataldo, in *Medicinal chemistry and pharmacological potential of fullerenes and carbon nanotubes*, ed. F. Cataldo and T. Da Ros, Springer, Dordrecht, Netherlands, 2008, pp. 317-335.
- 24 B. Alp and S. Cesur, *J. Appl. Polym. Sci.*, 2013, **130**, 1259-1275.
- 25 S. Abbott, C. M. Hansen and R. S. Valpey III., in *Hansen solubility parameters in practice*, Hansen-Solubility.com, 2008, pp. 66-69.

26 K. Adamska, A. Voelkel and K. Heberger, *J. Chromatogra. A*, 2007, **1171**, 90-97.

27 R. Hunt, in *Ure's dictionary of arts, manufactures, and mines*, Longmans, Green, and Co., London, England, 4th edn., 1878.