



# The role of surfactants on ethylcellulose oleogel structure and mechanical properties



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## ABSTRACT

The effects of surfactant addition to ethyl-cellulose (EC) based oleogels were examined with respect to the chemical nature of the “head” and “tail” groups of the surfactant. Unique sigmoidal temperature dependent rheological behavior was observed upon surfactant addition, suggesting additional organized structure formation. Glycerol-based surfactant addition lead to greatest decrease in the sol–gel and gel–sol transition temperatures compared to sorbitan-based surfactants. This behavior can be attributed to the plasticizing nature of the small head group of glycerol compared to the larger head group of sorbitan surfactants. A significant increase in the penetration force of the gels was observed upon surfactant addition, suggesting possible surfactant–polymer interactions which stiffen the polymer network. Thermal analysis detected a reduction in both SMS and GMS crystallization peak temperature and enthalpy. In the case of GMS, two melting peaks were observed upon EC addition to the oil phase, suggesting EC/surfactant interactions. These results demonstrate the effects of surfactant head group structure on EC oleogel rheological properties.

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## 1. Introduction

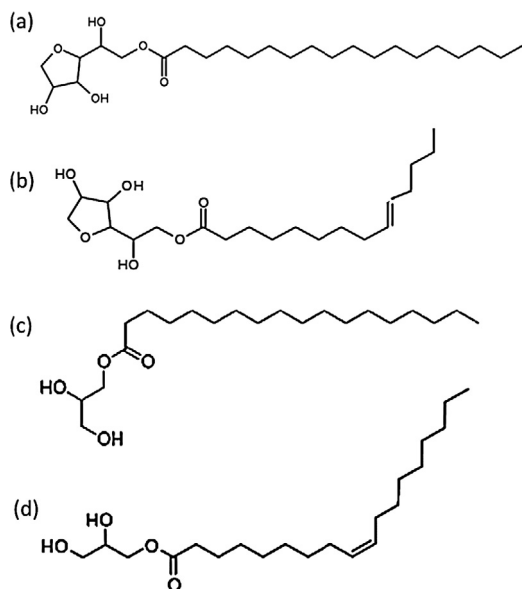
In the past decade oleogels have been proposed as a way to structure oil in various applications such as personal care, pharmaceutical and food products (Marangoni & Garti, 2011). Oleogel formation is achieved due to the addition of structuring agent, termed gelator, to the liquid oil phase. Gelator molecules usually self-assemble to create a three dimensional network which stabilizes the oil phase due to the formation of physical bonds such as Van der-Waals and hydrogen bonds which promote crystallization, cross-linking and stacking. Several types of gelators can be found in the literature: crystalline particles or fibrils, Liquid crystalline mesophases, jammed particle systems, and macromolecular gels. To date, only one food grade polymer, ethyl-cellulose (EC), has been reported to directly gel triglyceride oils (Marangoni, 2010b). Other polymer based oleogel systems involve an indirect entrapment of liquid oil by creating dried polymer network which then absorb liquid oil to create the final oleogel system. This type of systems found in the literature is based on proteins (Mazzenga, 2011; Romoscanu & Mezzenga, 2006), polysaccharides (Patel et al., 2014; Patel, Schatteman, Lesaffer, & Dewettinck, 2013)

and polysaccharide/protein mixtures (Patel et al., 2015). EC is a linear polysaccharide which shares the same polymer backbone as cellulose with the replacement of some of the hydrogen atoms of the hydroxyl end-groups with ethane end-groups thus chemically it can be classified according to the degree of substitution (DS) along the polymer backbone. Water solubility is achieved with DS in the range of 1.0–1.5 while solubility in organic solvents is achieved with DS values in the range of 2.4–2.5 (Kosh, 1937). EC gelation in oil phase is achieved after mixing the polymer powder with the oil phase, increasing the temperature above the polymer glass transition, approximately 140 °C, followed by cooling below the gel point temperature. Both the glass transition and the gel point are directly correlated to the polymer molecular weight (Davidovich-Pinhas, Barbut, & Marangoni, 2015).

EC based oleogels have shown promise as an oil structuring agent in many applications such as replacement of fats in foods (Marangoni, 2010b), heat resistance agents in chocolate (Marangoni, 2010a), oil binding agents in bakery products (Cattaruzza, Radford, & Marangoni, 2012), and as the basis for cosmetic pastes (Marangoni, 2012). Recent studies have shown the effects of various factors on EC oleogel mechanical properties, including solvent polarity, cooling rate, fatty acid and fatty alcohol addition, etc. (Davidovich-Pinhas, Gravelle, Barbut, & Marangoni, 2015; Gravelle, Davidovich-Pinhas, Zetzel, Barbut, & Marangoni, 2015). The effects of solvent polarity, external factors and minor

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**Fig. 1.** Schematic illustration of (a) sorbitan monostearate (SMS), (b) sorbitan monooleate (SMO), (c) glycerol monostearate (GMS), and (d) glycerol monooleate (GMO).

component addition can be explained from the fact that EC forms a hydrogen bond stabilized polymer network in the oil. More specifically, the balance between polymer–solvent and polymer–polymer interactions in the system play a major role on the network structure and gel properties.

Recent work from our laboratory (Gravelle, Barbut, Quinton, & Marangoni, 2014) have shown the plasticizing effects of sorbitan monostearate (SMS) and glycerol monooleate (GMO) addition to the mechanical strength of EC based oleogels. In this work, it was demonstrated that addition of surfactants provides a useful way to manipulate the mechanical properties of EC gels. However the mechanism by which these surfactant molecules interact with the EC network and their role in the strength enhancement remains unexplained.

This research aims to characterize the effects of surfactant addition on ethyl-cellulose/canola oil oleogel mechanical strength. Four different surfactants were studied having similarity in their chemical structure, sorbitan monostearate (SMS) (Fig. 1a), sorbitan monooleate (SMO) (Fig. 1b), glycerol monostearate (GMS) (Fig. 1c), and glycerol monooleate (GMO) (Fig. 1d). The surfactants were chosen in order to examine the role of both the “head” and “tail” groups on the final gel properties.

## 2. Material and methods

### 2.1. Materials

Ethyl-cellulose (EC), Ethocel®, was purchased from Dow Chemicals Company (Midland, MI, USA) and used as received. EC 45 cP with molecular weights of  $72.8 \pm 15$  kDa (Davidovich-Pinhas, Co, Barbut, & Marangoni, 2014) was used. Canola oil (No Name®, Loblaw's Inc., Toronto, Ontario, CA) was obtained from the local supermarket and stored at 4°C. The surfactants glycerol monooleate (GMO), sorbitan monooleate (SMO), glycerol monostearate (GMS) and sorbitan monostearate (SMS) were purchased from HallStar (Bedford Park, IL, USA), Sigma-Aldrich Ltd. (Oakville, Ontario, Canada), Caravan Ingredients (Lenexa, KS, USA) and Danisco A/S (Scarborough, ON, CA), respectively. The antioxidant butylated hydroxytoluene (BHT) was obtained from Spectrum

Chemical Manufacturing Corporation (New Brunswick, NJ, USA), and used as received.

### 2.2. Rheological analysis

Rheology experiments were performed using an Anton Paar MCR320 rheometer (Anton Paar, Saint Laurent, Canada) equipped with a temperature control unit using a 50 mm cone and plate (2° angle) configuration.

Samples were prepared by mixing 11 wt.% EC and 3.67 wt.% surfactant in canola oil (CO) to total weight of 10 g. Based on previous work, the above EC and surfactant concentrations give a consistent and stable gel formulation with a detectable effect of surfactant addition on the gel properties. Samples were placed on a magnetic hot plate and mixed at 300 rpm while heated to  $\sim 150^\circ\text{C}$ . After complete dissolution of the EC powder in the canola oil, the samples were poured onto a preheated ( $150^\circ\text{C}$ ) rheometer plate.

The oleogel cross-over behavior and gel strength were analyzed using temperature sweep experiments in the range of  $60\text{--}150^\circ\text{C}$ . All experiments were conducted using a frequency of  $30\text{ rad s}^{-1}$  and a % strain within the linear viscoelastic region (LVR) of each sample (determined prior with strain sweep experiments at the temperature range mentioned above). Each experiment was performed as a cycle of cooling, heating and cooling using  $10^\circ\text{C min}^{-1}$  cooling/heating rate. The data presented is the average of three replicates.

Gel point temperatures were determined using frequency sweep experiments at different temperatures. The experiments were conducted in the range of  $10\text{--}100\text{ rad s}^{-1}$  using % strain at the LVR (according to strain sweep experiments conducted at the same temperature range mentioned above).

In all experiments, samples were poured on the pre-heated rheometer lower plate ( $150^\circ\text{C}$ ), followed by lowering the upper cone plate to fixed distance of 0.207 mm. Samples were allowed to equilibrate at  $150^\circ\text{C}$  for 5 min prior to the start of the experiment.

### 2.3. Gel preparation for mechanical analysis

EC oleogels were prepared following a protocol developed previously in our laboratory (Gravelle et al., 2014). The EC–oil–surfactant mixture was heated in a bench-top gravity convection oven (Fisher Scientific) set to approximately  $170^\circ\text{C}$ . Throughout the heating process, the solution was mixed with an overhead mechanical stirrer (model L1U10F Lightnin LabMaster, Wytheville, VA, USA) and a long shafted stirring rod with a high shear radial flow impeller, which was fed through a hole in the roof of the oven. Temperature was monitored with a thermocouple unit (model 800024, Sper Scientific, Scottsdale, AZ, USA) to note the onset of the glass transition temperature ( $T_g$ ) of EC ( $\sim 140^\circ\text{C}$ ). After the  $T_g$  was reached, the solution was left for an additional 10 min to facilitate complete softening of the polymer. The entire heating process took 45–50 min, and the final temperature of the molten gel was approximately  $150^\circ\text{C}$ . After heating, the sample was removed and split into six aliquots of  $\sim 35$  ml each in 50 ml polypropylene centrifuge tubes (Fisher Scientific). The molten gels were then moved to a  $25^\circ\text{C}$  incubator for storage for approximately 24 h prior testing. The anti-oxidant BHT was added to all samples at a 0.01% level to minimize oxidation effects.

### 2.4. Mechanical properties

The large deformation mechanical properties of EC oleogels were evaluated using a back extrusion experiment following the experimental set-up demonstrated by Gravelle et al. (Gravelle et al., 2014). Tests were performed using a texture analyzer model TA.XT2 (Stable Micro Systems, Texture Technologies Corp., Scarsdale, NY,

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