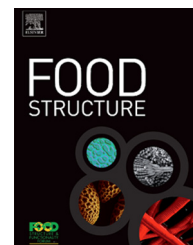


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# Microstructure of ethylcellulose oleogels and its relationship to mechanical properties

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## ABSTRACT

Small deformation rheology was used at a controlled strain of 0.05% and frequency from 1 to 100 Hz to obtain  $G'$ ,  $G''$ , and  $\tan(\delta)$  values for ethylcellulose oleogels of various compositions. Significant increases in both  $G'$  and  $G''$  were noted in oleogels prepared with 100 cP ethylcellulose as compared to 45 cP, yet no significant differences in  $\tan(\delta)$  were observed among gels containing the same type of vegetable oil. Oleogels prepared with increasing polymer concentration showed a significant increase in  $G'$  only when the concentration exceeded 13%. When the surfactant sorbitan monostearate was incorporated at a level of 3.33%, a significant increase in  $\tan(\delta)$  was seen, indicating a decrease in elasticity of these oleogels. Cryo-scanning electron microscopy was successfully utilized to image the internal polymer network of ethylcellulose oleogels, which contained small oil-filled pores of approximately 3.0–4.5  $\mu\text{m}$  in size lying between the interconnected polymer chains. Decreases in pore sizes were observed with increasing polymer concentration, oil unsaturation, and high levels of surfactant incorporation. No significant change in pore size was seen among gels made with different polymer viscosities, signifying an alternate mechanism for changing oleogel hardness. De-oiled ethylcellulose oleogels were also successfully imaged using fluid-phase contact mode atomic force microscopy. The striking similarity in the images obtained by both these methods strongly suggests the morphological features of the oleogels are preserved through the sample preparation procedure. Ethylcellulose xerogel micrographs were shown for the first time, and also contain some regions with pores similar in morphology to those identified in micrographs of the partially de-oiled oleogels.

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## 1. Introduction

The potential for structuring edible oils using food grade ingredients has become an active area of research over the past decade, with the first publications in this area appearing in literature around 2004 (Gandolfo, Bot, & Flöter, 2004; Ojijo, Neeman, Eger, & Shimoni, 2004). A number of promising

oleogelators have now been identified and continue to be actively investigated. These molecules can generally be divided into three main gelation strategies; the formation of a network of crystalline particles, self-assembled fibrillar networks, and polymer gelation (Bot, Veldhuizen, den Adel, & Roijers, 2009; Co & Marangoni, 2012; Pernetti, van Malssen, Flöter, & Bot, 2007; Rogers, 2009). Oleogelators which impart structure through the formation of a crystal network include

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waxes, such as candelilla (Alvarez-Mitre, Morales-Rueda, Dibildox-Alvarado, Charo-Alonso, & Toro-Vazquez, 2012; Alvarez-Mitre, Toro-Vazquez, & Moscota-Santillan, 2013), rice bran (Dassanayake, Kodali, Ueno, & Sato, 2010; Hwang, Kim, Singh, Winkler-Moser, & Liu, 2012; Hwang et al., 2013), sunflower (Hwang et al., 2012, 2013), and shellac wax (Patel, Schatteman, De Vos, Lesaffer, & Dewettinck, 2013), among others. Some other examples of oleogelators which fall under this category include monoacylglycerides (Ojijo et al., 2004), ceramides (Rogers, Wright, & Marangoni, 2009), mixtures of lecithin with other surface active molecules (Nikiforidis & Scholten, 2014), and fatty acids, fatty alcohols, or combinations thereof (Gandolfo et al., 2004; Lupi et al., 2013). The formation of a 3-dimensional network in vegetable oils via the self-assembly of small molecules has been achieved using low concentrations (~2% or less) of ricinoleic acid (Wright & Marangoni, 2006), 12-hydroxy stearic acid (Rogers, Wright, & Marangoni, 2008) and combinations of phytosterols and oryzanol (Calligaris, Mirolo, Da Pieve, Arrighetti, & Nicoli, 2014). In terms of polymer oleogelators, ethylcellulose (EC), and more recently, hydroxypropyl methylcellulose (Patel, Schatteman, Lesaffer, & Dewettinck, 2013) have been identified as having the ability to impart structure on edible oils. However, no oleogels have thus far been incorporated into commercial food products. Additionally, existing organogelators are either extremely expensive, unsuitable for use in foods, or possess a major flaw, such as the resulting oleogel having extreme shear sensitivity thus making their addition in food systems very challenging, if not impossible (Bot & Flöter, 2011; Co & Marangoni, 2012; Hughes, Rush, & Marangoni, 2011). In this light, the discovery of EC as an organogelator was a step forward, as it is commercially available, inexpensive relative to many highly purified organogelators, and is also considered food grade or near-food grade, depending on the country or organization in question (Zetzel & Marangoni, 2014). For example, the Food and Agriculture Organization of the United Nations, in collaboration with the World Health Organization, has listed EC as a food additive that may be used in a variety of foods under the conditions of good manufacturing practices, as outlined in the Preamble of the Codex GSFA (FAO & WHO, 2012). This Preamble lists over 60 different food applications for EC, including confectionery products, fat spreads, fat emulsions, cheeses, poultry and game products, processed comminuted meat, and batters. The effectiveness of EC oleogels has already been shown in a variety of different food products, including chocolate, cookies, cream fillings, comminuted meat products and ground meat products (Stortz & Marangoni, 2011; Stortz, Zetzel, Barbut, Cattaruzza, & Marangoni, 2012; Zetzel & Marangoni, 2014; Zetzel, Marangoni, & Barbut, 2012). In most of these products, oleogels are used as a substitute for the traditionally used fat source. The primary goal of incorporating these oleogels is to mimic the functional properties of a solid fat, while reducing the level of saturated fat and eliminating any *trans* fatty acids. Overall, great improvements in the fatty acid profiles of food products can be achieved, while maintaining overall textural and mechanical properties. Additionally, the possibility of using these oleogel systems for delivery of lipid-soluble nutraceuticals

has recently been discussed, and could greatly expand their applications (Zetzel & Marangoni, 2012).

Outside of food systems, the mechanical properties of oleogels have been studied in detail. The texture profile analysis results of Laredo, Barbut, and Marangoni (2011) demonstrated a relationship between the level of unsaturation in the solvent (vegetable oil) and the resulting hardness of the oleogel; specifically, oils with a higher degree of unsaturation produce harder gels. This finding has since been confirmed in subsequent studies (Dey, Kim, & Marangoni, 2011; Zetzel et al., 2012). Additionally, increasing polymer content and the use of higher viscosity versions of EC have also been shown to strongly correlate with oleogel strength (hardness) (Dey et al., 2011; Zetzel et al., 2012).

In comparison to the studies on mechanical properties, there have been few attempts to reveal the underlying microstructure of the EC polymer network. The first reported images of EC oleogels were published by Laredo et al., using cryo-scanning electron microscopy (cryo-SEM; Laredo et al., 2011). Oleogels were made using an exceedingly high concentration of EC and were freeze-fractured in an attempt to reveal the internal polymer network. By using an excess of gelator, it was believed that any polymer supramolecular structure would be easier to identify. Unfortunately, these images did not exhibit any definitive features or structural elements which would provide more information about the organization of the polymer network within these gels.

The work of Dey et al. also utilized cryo-SEM in an attempt to image EC oleogels. This group, however, did not perform any freeze fracturing of the samples, and instead soaked the gel in a solvent solution (0.2 g oleogel in 40 mL 90:10 vol/vol 2-butanol/methanol) in an attempt to remove surface oil and expose the polymer network. While they were able to identify a positive correlation between gel strength (storage modulus) and both oil globule size and polymer strand thickness, the large volume of solvent utilized likely had a significant effect on the structure and properties of the imaged surface. Additionally this relationship was established using a small sample size of only 25 measurements per treatment. While there appears to be a strong relationship between microstructure and the mechanical properties of these gels, the ingredient components used to make oleogels for each storage modulus were not listed. It is hypothesized that several factors, such as the presence of a surfactant, polymer concentration, or changes in molecular weight, may affect the storage modulus through different mechanisms. If any differences were present, they were not immediately apparent.

In a subsequent study, our group used a modified version of the technique employed by Dey et al. (2011) so that only a small amount of solvent was dropped over the sample surface (Zetzel et al., 2012). This modification allowed for the removal of surface oil from the oleogel, while minimizing any structural changes to the sample. This work provided the first micrographs of what is believed to be the EC network as it is arranged within the gel. These micrographs show a coral-like network of polymer strands or bundles, surrounding pores of varying sizes which would have been filled with liquid oil prior to solvent extraction (Zetzel et al., 2012). Though this technique allows only the oleogel surface to be viewed, we believe that this network is continuous throughout the samples, meaning

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