



Influence of solvent quality on the mechanical strength of ethylcellulose oleogels



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ABSTRACT

Ethylcellulose (EC) is the only known food-grade polymer able to structure edible oils. The gelation process and gel properties are similar to those of polymer hydrogels, the main difference being the nature of the solvent. The present study examines the influence of solvent quality on the large deformation mechanical behavior of EC oleogels. Two alternative strategies for manipulating the mechanical response of these gels were evaluated; manipulating the bulk solvent polarity and the addition of surface active small molecules. Gel strength was positively correlated to solvent polarity when blending soybean oil with either mineral oil or castor oil. This behavior was attributed to the ability of the polar entities present in the oil phase to interact with the EC gel network. The addition of the small molecules oleic acid and oleyl alcohol resulted in a substantial enhancement in gel strength up to 10 wt% addition, followed by a gradual decrease with increasing proportions. Binding interactions between EC and these molecules were successfully modeled using a Langmuir adsorption isotherm below 10 wt% addition. Furthermore, the thermal behavior of stearic acid and stearyl alcohol also indicated a direct interaction between these molecules and the EC network. Differences in the mechanical behavior of gels prepared using refined, bleached, and deodorized canola or soybean oils, and those made with cold-pressed flaxseed oil could be attributed to both oil polarity, and the presence of minor components (free fatty acids). Shorter pulsed NMR T_2 relaxation times were observed for stronger gels due to the more restricted mobility of the solvent when interacting with the polymer. This work has demonstrated the strong influence of the solvent composition on the mechanical properties of EC oleogels, which will allow for the tailoring of mechanical properties for various applications.

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1. Introduction

Many of the functional attributes of fats are derived from the presence of a triacylglycerol (TAG) crystal network which provides mechanical strength and other functional attributes. In these fats, the liquid oil component is stabilized by a three-dimensional hierarchical network of crystalline TAGs which are predominantly made up of saturated or *trans* fatty acids (Marangoni et al., 2012). When these TAGs solidify, they assemble into crystalline lamellae which epitaxially stack to form crystalline nano-platelets (CNPs).

These CNPs represent the basic building blocks of the fat crystal network, which then assemble into larger aggregates to eventually form meso-scale fractal structures (flocs). The assembly of these structures then forms the three-dimensional network of solid material which is able to bind the liquid oil component. However, the crystallization process, and consequently, the functional properties of such fats can be strongly influenced by factors such as fatty acid composition and processing conditions (Marangoni, 2012).

The growing stigma against saturated fats due to rising obesity rates and associated metabolic disorders has led to a substantial push for the development of alternatives to these types of traditional fats. The positive health benefits attributed to unsaturated fats, such as those found in many plant-based oils, has spurred an interest in oil-based fat substitutes. The main alternative strategy which has been investigated over the past decade to structure liquid oils and impart solid-like functional characteristics has been through the use of oleogelators. The study of oleogels

Abbreviations: CNP, crystalline nanoplatelet; CPMG, Carr-Purcell-Meiboom-Gill; DSC, differential scanning calorimetry; EC, ethylcellulose; FFA, free fatty acid; FID, free induction decay; NMR, nuclear magnetic resonance; TAG, triacylglycerol; TPC, total polar components.

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targeted toward edible, pharmaceutical and cosmetic applications has become a very active field in recent years and has led to the identification of a variety of gelators (Bot, Veldhuizen, den Adel, & Roijers, 2009; Co & Marangoni, 2012; Perneti, van Malssen, Flöter, & Bot, 2007). The ability of these molecules to structure oil can generally be categorized into three main strategies. These include the formation of a network of crystalline particles, low molecular weight oleogelators which form self-assembled fibrillar networks, and polymer gelators. Recently, the use of several water-soluble polymer systems to stabilize oil through indirect, multi-step templating approaches has been demonstrated using several natural or chemically modified bio-based polymers, or combinations thereof (Patel et al., 2014, 2015; Patel, Schatteman, Lesaffer, & Dewettinck, 2013). However, to date the only direct approach for producing polymer based oleogels is through the use of ethylcellulose (EC), a chemically modified derivative of the naturally occurring polymer cellulose. EC is commercially available on an industrial scale, has GRAS (generally regarded as safe) status, and is currently used in a variety of industrial applications. Commercial versions of EC are manufactured to have a degree of substitution of ~ 2.5 . This level of substitution imparts unique properties on the polymer, such as solubility in a variety of organic solvents, and also results in a depression in the polymer's glass transition temperature (T_g) to approximately 135 °C (Davidovich-Pinhas, Barbut, & Marangoni, 2014; Dow Cellulosics, 2005). When heated above this temperature, the polymer can be dispersed in mixtures of liquid TAGs. Upon re-cooling, inter-polymer junction zones are created through the formation of hydrogen bonds between the unsubstituted hydroxyl groups, resulting in an entangled network of polymer strands which entrap the oil, forming a physical gel (Davidovich-Pinhas, Barbut, et al., 2015; Laredo, Barbut, & Marangoni, 2011).

The mechanical properties of edible oil-based EC oleogels can be manipulated by adjusting a variety of parameters, such as the type of oil used, the molecular weight and concentration of EC employed, as well as through the addition of various surfactants (Gravelle, Barbut, Quinton, & Marangoni, 2014; Laredo et al., 2011; Zetzi et al., 2014; Zetzi, Marangoni, & Barbut, 2012). The influence of molecular weight and EC concentration levels have previously been addressed (Gravelle et al., 2014), and can be explained in terms of the interconnectivity of the network and the extent of inter-polymer interactions. In contrast, although the influence of solvent composition has been recognized, a coherent study on the factors affecting gel strength has not yet been published. For example, the influence of oil type has been attributed to the composition of the TAG molecules which make up the oil phase, as it has been seen that oils rich in more highly unsaturated fatty acids produce firmer gels (Laredo et al., 2011). In addition, the presence of polar materials, either arising from the onset of lipid oxidation or through the addition of oils with polar functional groups, has also been shown to have a reinforcing effect on gel strength (Gravelle, Barbut, & Marangoni, 2012, 2013). Finally, the presence of surface-active small molecules have been reported to substantially modify the properties of EC oleogels (Davidovich-Pinhas, Gravelle, Barbut, & Marangoni, 2015; Gravelle et al., 2014), however their influence appears to be highly dependent on the structure of the specific molecule employed.

In light of these observations, the goal of the present work is to characterize the influence of solvent quality on the mechanical properties of EC oleogels in an attempt to elucidate the molecular interactions responsible for these effects. In the present work we have grouped the aforementioned parameters into two main strategies for modifying the mechanical properties of EC oleogels: (i) the influence of bulk solvent polarity and (ii) the presence of surface-active small molecules which may directly interact with the EC network.

2. Materials and methods

2.1. Materials

Refined, bleached, deodorized (RBD) canola oil and soybean oil, cold-pressed flaxseed oil and USP grade castor oil were purchased from a local grocery market. Mineral oil (paraffin oil, heavy) and oleic acid (>97%) were purchased from Fisher Scientific (Ottawa, ON). Oleyl alcohol (technical grade, >60%) was obtained from Sigma-Aldrich Canada Ltd. (Oakville, ON). 45 cP EC (ETHOCEL™ std. 45, Dow Wolff Cellulosics) was purchased through a local supplier. Butylated hydroxytoluene (BHT) was obtained from Spectrum Chemical Manufacturing Corporation (New Brunswick, NJ). All chemicals required for the evaluation of primary oxidation byproducts and the removal of free fatty acids were purchased from commercial sources.

2.2. Quantification of oxidative byproducts

Oxidation of the vegetable oils was monitored both before and after heating. Oxidation of the oil component in the oleogels was inferred by mimicking the gel preparation procedure; a 275 g batch of oil was heated to ~ 150 °C under continuous mixing and subsequently cooled to room temperature. No antioxidant was added to the oils analyzed for the development of oxidative byproducts. The extent of lipid oxidation was evaluated according to the content of primary oxidation byproducts, as determined by the AOCS acetic acid-isooctane method (AOCS Official Method Cd 8b-90, 1996). Briefly, an aliquot of each oil was dissolved in 50 ml of a 3:2 acetic acid-isooctane solution. 0.5 ml of a saturated potassium iodide solution was then added, followed by 1 min of thorough mixing and immediate addition of 30 ml distilled water. The solution was then titrated with 0.1 M sodium thiosulfate until yellow iodine color had nearly faded. Finally, 0.5 ml of both a 10% sodium lauryl sulfate solution and starch indicator solution were added to the test fraction and the titration was continued to completion. Peroxide values were reported as milli-equivalents of peroxides present per kilogram of oil (mequiv. kg^{-1}). All treatments were repeated in duplicate.

2.3. Evaluation of solvent polarity

The percent total polar components (%TPC) in the oils were monitored as an additional polar indicator of the progression of oxidation. Polarity was evaluated using a commercially available testing unit commonly used to monitor the degradation of frying oils (Testo® 270 Deep-frying Oil Tester, Testo Inc., Sparta, NJ). Each test portion was pre-heated and measured at 50 °C, as this unit was designed to operate over the range of 40–200 °C. This unit reports the polarity of the TAG solution as the %TPC, as determined by a capacitance measurement. In addition, the polarity of soybean oil was manipulated by supplementation with either castor oil or mineral oil. The dose-response effect of incorporating these additives was also evaluated via the %TPC, measured in the absence of EC.

2.4. Determination of free fatty acid (FFA) content

The FFA content was determined for both fresh and heated versions of canola, soybean, and flaxseed oils (AOCS Official Method Ca 5a-40, 2009). Briefly, a portion of each oil was mixed with 50 ml of warmed, neutralized ethanol (95%, Fisher Scientific) containing a small amount of phenolphthalein indicator (Sigma-Aldrich), so as to dissolve the FFAs. The mixture was then titrated to completion against a 0.1 N sodium hydroxide solution and the FFA content was calculated as oleic acid. All treatments were repeated in duplicate.

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