Effect of ethylcellulose on the structure and stability of non-aqueous oil based propylene glycol emulsions

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ABSTRACT

The hydrophobic polymer ethylcellulose (EC) has been used to structure vegetable oils and as a stabilizer of oil/water (o/w) emulsions, among other non food uses. In this work we show that EC dissolved in medium chain triglycerides (MCT) or soybean oil (SO) is able to stabilize non-aqueous emulsions of propylene glycol (PG) as a dispersed phase. Cream-like emulsions can be obtained at both low and high homogenization speeds which show a very good stability for at least one month without the requirement of co-surfactants. PG-in-oil emulsions at concentrations of EC below 5% (w/w) display pseudoplastic behavior and greater viscosity than the respective solutions of the polymer in MCT or SO. However, at concentrations of EC above 5% (w/w) firm gels are formed in MCT or SO and after the addition of PG, the emulsions formed have lower viscosity than the original solutions of the polymer in MCT or SO. Such effects were independent of the mean molecular weight (MMW) of the EC at high shear stress and inversely proportional at low shear stress. These results indicate that the stabilizing effect of EC in PG-in-oil emulsions might not be caused mainly by an increase in the viscosity of the continuous phase. Comparing all the results obtained, we can infer that EC, despite being insoluble in PG, is promoting interactions which are responsible for the observed effects.
These PG-in-oil emulsions have interesting structural and flow properties which make them attractive to be used in food formulations, either as emulsions themselves or as potential vehicles for active ingredients.

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1. Introduction

The past several decades have seen a change in the main causes of death and physical impairment. Until the mid-twentieth century, infectious diseases were the main cause of death. However, nowadays we are challenged by a group of chronic pathologies such as atherosclerosis, obesity, diabetes and cancer, most of which are somehow related to nutrition habits and lifestyle (Kohn, 2008; W. H. O., 2008). In this context, governments across the world are concerned with the deleterious health effects of the increased consumption of high-fat diets. The difficulty in reducing fat ingestion arises mainly from the fact that saturated fats contribute to many of the important organoleptic properties of foods, including palatability, lubrication and structure.

Moreover, there is a growing tendency to incorporate special nutrients into the diet as a strategy to control metabolic related diseases. Therefore, any attempt to reduce the fat content of foods has to take into account not only its possible effect on food structure and taste, but also the fact that many important nutrients and functional ingredients are water-insoluble (i.e.: flavonoids, fatty acids, lutein, phytosterols, etc.).

One strategy that has been recently explored is to replace trans and saturated fat by unsaturated oils structured as organogels by the use of hydrophobic polymers like ethylcellulose (EC) (Gravelle, Barbut, & Marangoni, 2012; Marangoni, 2009, 2010; Zetzl, Marangoni, & Barbut, 2012). Related to this, Golding and Pelan (2010), highlight the relevancy that emulsifiers have as structuring tools for fat reduction and/or nutritional enhancement in many food products.

In this context, different authors have investigated the use of EC for its application in various aspects of the food and pharmaceutical industries. Such applications include its use as a stabilizer of water in oil (w/o) emulsions (Hasenhuettl, 2010b; Melzer, Kreuter, & Daniels, 2003), as a suspension stabilizer (Do, Mitchell, Wolf, & Vieira, 2010), for microparticle manufacturing (Alhnan & Basit, 2011) and as an

organogelator for vegetable oils (Aiache, Gauthier, & Aiache, 1992; Almeida & Bahia, 2006; Gravelle et al., 2012; Zetzl et al., 2012).

Related to the emulsions in foodstuffs, the oil in water (o/w) emulsions are the most frequent type of aggregation structures, and there is abundant research into their production as well as their stabilization mechanisms (Ushikubo & Cunha, 2014). However, there are comparatively few works on liquid w/o emulsions, which generally present low stability because of the high mobility of water droplets, as a result of what they can easily sediment, flocculate or coalesce (Melzer et al., 2003; Ushikubo & Cunha, 2014).

One category of emulsions that have been rarely studied are the non-aqueous emulsions, also designated as oil-in-oil, anhydrous or waterless emulsions. Although the first researches in this topic appeared in the literature around 50 years ago (Petersen & Hamill, 1968) most of the investigations since then have been focused on cosmetic formulations and drug delivery systems (Suitthimeathegorn, Jaitely, and Florence (2005), Atanase and Riess (2013) and references therein).

Related to foodstuffs, Patel, Schmid, and Lawrence (2006) prepared microemulsions in which water was replaced with non-aqueous polar solvents such as glycerol or propylene glycol (PG) using soybean lecithin as a surfactant. From ternary phase diagrams it was observed that oil-in-PG emulsions, with diverse structural characteristics, are favored by the solubility properties of soybean lecithin in the PG phase. However, a co-surfactant was always required to obtain stable emulsions (Patel et al. (2006). Another aspect that has to be considered is that most of the soybean lecithin that is produced worldwide comes from genetically modified soy. Since traces of DNA have been detected in soybean lecithin, the demand of non-GMO lecithin has been growing, especially in the European Union. As there is an important concern of a lack of supply of non-GMO lecithin, several suppliers and consumers are looking at soy lecithin alternatives.

In the search for alternatives to stabilize non-aqueous oil based emulsions, the effects of EC in PG-in-oil emulsions were studied. The stability and structure of PG emulsions in medium- and longchain triglycerides and their dependency on the concentration and molecular weight of EC were evaluated. The macro and micro structure as well as the flow properties of the resultant aggregation structures were characterized.

2. Materials and methods

2.1. Materials

EC polymers of different molecular weights (Ethocel™ Standard Premium 10, 20, 45 and 100) with ethoxyl content between 48.0% and 49.5% (supplier information) were kindly provided by Dow Chemicals, Brazil.

Medium chain (caprylic/capric) triacylglycerol (MCT) oil (Neobee™ M-5) was obtained from Stepan Co (USA). This oil contains 98% of a mixture of C8:0 and C10:0 fatty acids (66% and 32% respectively).

Pure soybean oil (SO) (Sojola, AGD, Argentina) was obtained from a local supermarket one day before preparing the solutions of EC.

Propylene glycol (PG) and analytical grade methylene blue were from Cicarelli (Rosario, Argentina).

Polyglycerol polyricinoleate (PGPR) (Danisco, Denmark).

2.2. Methods

2.2.1. Standard procedure for the preparation of EC solutions in oils

EC and oil (SO or MCT) were weighed and mixed into 250 mL erlenmeyers at room temperature, and then heated with constant stirring during 5 min on a hot plate (Thorbell; Argentina) provided with a digital temperature probe previously set at 90 °C, in order to achieve a homogenous suspension. Then, the temperature was increased until the EC glass transition temperature (Tg) was reached (between 130 °C and 150 °C, depending on the MMW (mean molecular weight) of the polymer), which occurred within 10 min. According to our experience, all EC polymers in 50 g mixture batches give a clear solution in less than 5 min after the Tg is reached.

The solutions, still hot and with a concentration higher than 6% (w/w) of EC, were slowly poured into three plastic cylindrical vials, placed in an incubation oven set at 20 °C (Shel Lab; USA) and left there for 1 h. Thereafter, vials were transferred to a refrigerator at 4 °C where they were stored for 24 h before testing. These samples were tested via the back extrusion assay (Section 2.2.4). The solutions of EC with concentrations below 2% (w/w) were left to reach, and then maintained at room temperature. These samples were tested using a rheometer (Section 2.2.3).

2.2.2. PG/oil emulsion preparation procedures

The oleogels prepared in Section 2.2.1 were previously melted at 80 °C as to make them fluid and easy to mix and then PG was slowly added while the solution was mixed either vortexing at 3200 r.p.m. (Vortex-Genie 2; Scientific Industries Inc.; USA) or homogenizing using a rotor-stator homogenizer at 8000 r.p.m. (Ultra Turrax; Janke & Kunkel; Germany). After reaching the final proportion of PG (10, 30 and 50% (w/w)) PG mixing was maintained during 1 min.

2.2.3. Flow measurements

The physical characteristics of the solutions of EC with concentrations lower than 2% (w/w) and the resulting PG-in-oil emulsions, were evaluated by means of steady flow analysis (Ruíz Martínez, Muñoz de Benavides, Morales Hernández, & Gallardo Lara, 2003), which was performed at 25 °C in a controlled stress rheometer (Physica MCR 301; Anton-Paar; Austria) with a cone-plate (CP50-1) measuring system. This method was chosen because of the low consistency of the samples. In order to gain access to the properties of the solutions that form rigid gels at room temperature, the rheological measurements of EC solutions with 4–23% (w/w) EC were also evaluated but at 40 °C, with shear rates from 2 to 50 1/s.

Prior to each measurement, samples were pre-sheared with a 100 Pa stress for 3 min, and left to equilibrate for the same time. After that, samples were subjected to a shear stress ramp between 0.1 Pa and 50 Pa. The resulting shear rate ($d\gamma/dt$) and dynamic viscosity (η) were measured. Results are the average of three measurements. Data are shown as mean values $\pm$ standard deviations. Statistical significance and differences among groups were determined by analysis of variance and Student–Newman–Keuls test. – < 0.05 values were considered statistically significant.

2.2.4. Back extrusion measurements

The structural characteristics of the EC solutions at concentrations higher than 6% (w/w) and the resulting PG-in-oil emulsions, were

Table 1
Apparent viscosity at 40 1/s shear rate value for MCT-based oleogels prepared with different concentrations of four molecular weight of EC [a].

EC concentration (% w/w)	EC-10	EC-20	EC-45	EC-100
	(Pa s; mean $\pm$ SE for three measurements)			
4	0.20 $\pm$ 0.01	0.29 $\pm$ 0.01	0.38 $\pm$ 0.02	0.53 $\pm$ 0.02
5	0.33 $\pm$ 0.03	0.80 $\pm$ 0.04	1.37 $\pm$ 0.02	1.98 $\pm$ 0.18
7	0.58 $\pm$ 0.01	1.16 $\pm$ 0.02	2.56 $\pm$ 0.09	2.90 $\pm$ 0.12
9	1.24 $\pm$ 0.02	2.45 $\pm$ 0.03	4.43 $\pm$ 0.17	8.95 $\pm$ 0.39
12	3.26 $\pm$ 0.11	6.80 $\pm$ 0.32	13.76 $\pm$ 0.74	– [b]
17	12.30 $\pm$ 0.23	31.53 $\pm$ 1.16	27.48 $\pm$ 1.33	– [b]
23	64.16 $\pm$ 2.54	79.11 $\pm$ 2.15	– [b]	– [b]

[a] Measurements carried out at 40 °C.
[b] The elevated firmness of oleogels not permitted an adequate measurement in the rheometer because the cone slid on the surface of the sample preventing the cone–gel interaction needed to record the real shear stress.