



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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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.

Abbreviations: EC, ethylcellulose; MCT, medium chain triglycerides; SO, soybean oil; PG, propylene glycol; MMW, mean molecular weight; PGPR, polyglycerol polyricinoleate.

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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; Zetzel 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 (Suihthimeathegorn, 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.

Materials and methods

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.

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 ± SE for three measurements) | | | |
| 4 | 0.20 ± 0.01 | 0.29 ± 0.01 | 0.38 ± 0.02 | 0.53 ± 0.02 |
| 5 | 0.33 ± 0.03 | 0.80 ± 0.04 | 1.37 ± 0.02 | 1.98 ± 0.18 |
| 7 | 0.58 ± 0.01 | 1.16 ± 0.02 | 2.56 ± 0.09 | 2.90 ± 0.12 |
| 9 | 1.24 ± 0.02 | 2.45 ± 0.03 | 4.43 ± 0.17 | 8.95 ± 0.39 |
| 12 | 3.26 ± 0.11 | 6.80 ± 0.32 | 13.76 ± 0.74 | – ^b |
| 17 | 12.30 ± 0.23 | 31.53 ± 1.16 | 27.48 ± 1.33 | – ^b |
| 23 | 64.16 ± 2.54 | 79.11 ± 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.

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).

Methods

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 (T_g) 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 T_g 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).

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.

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 (Ruiz 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 (dy/dt) and dynamic viscosity (η) were measured. Results are the average of three measurements. Data are shown as mean values ± 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.

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

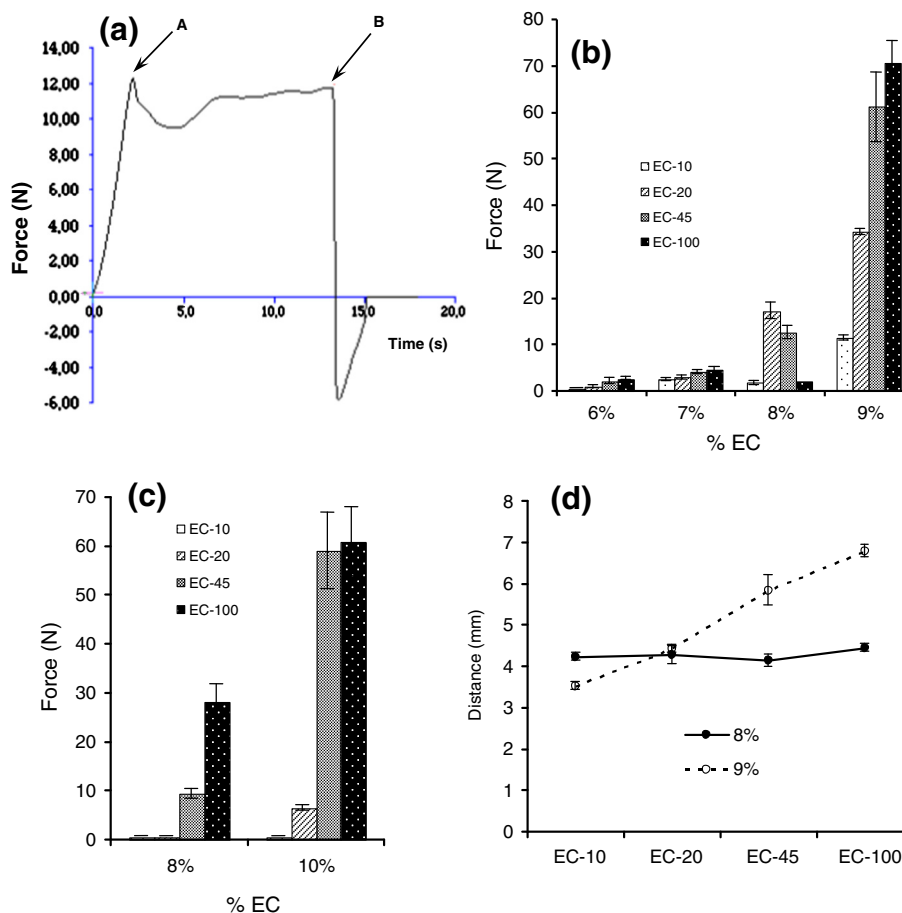


Fig. 1. (a) Typical back extrusion profile for a MCT oleogel obtained with 9% EC-10. Points A and B: see text for a detailed explanation. (b)–(c) Back extrusion force at maximum penetration distance (20 mm) for oleogel samples of ECs with different MMW, at different polymer concentrations in MCT and SO respectively. (d) Distance that back extrusion probe penetrates into the oleogel samples before the force at point A is reached in the test (see Fig. 1 (a)) for 8% and 9% of all ECs tested.

evaluated through a back extrusion technique (Zetzel et al., 2012) using a TA.XT2i texture analyzer (Stable Micro Systems; UK) with a plastic probe (P/0.5 HS), with cylindrical shaft and hemispherical tip (diameter = 13 mm). Although the probe and vials that contained the oleogels were smaller than those reported the relationship between probe and vial dimensions was the same (see Fig. S.1 in supplementary data). After 24 h storage at 4 °C, the probe was used to penetrate 20 mm into each sample at a rate of 1.5 mm/s, while measuring the resulting force response. All samples were tested in triplicate at 4 °C, and experimental error was ca. $\pm 5\%$.

Light microscopy

Taking advantage of the good solubility of methylene blue in PG and its insolubility in the MCT and SO, an aliquot of solid dye was dissolved in PG previous to emulsification into EC/oil mixtures.

The emulsions were prepared according to the methodology described in Section 2.2.2 and the resultant emulsions were observed in a light microscope (Axiovert 135 M) equipped with a digital camera (ERC5s) and an image processor software (ZEN 2011); (all devices from Zeiss; Germany).

Results and discussion

Effect of EC in the flow properties of MCT solutions

Several authors have been working on the characterization of EC solubility in different types of vegetable oils as well as in the rheological properties of the resultant oleogels and emulsions. Among these oils we can mention soybean, canola, rapeseed, olive, palm and flax oil, all of

them composed by long chain fatty acids (Gauthier, Aiache, & Aiache, 1994; Stortz, Zetzel, Barbut, Cattaruzza, & Marangoni, 2012). Although EC is relatively soluble in these oils, giving homogeneous solutions, it is frequently required to heat the samples for 30–45 min. With this procedure, it is common to observe that some undesirable compounds are generated. In an attempt to reduce heating time as a strategy to reduce the generation of off-flavors, we carried out the first experiments on solubilization of EC in MCT. These oils are attractive for food applications because they do not contain trans fatty acids and their saturated medium chain fatty acids are not derived from genetically modified organisms (for an extensive list of applications see: www.stepan.com). Furthermore, MCTs have a great oxidative stability, very faint color, characteristic slight taste and are essentially odorless. With MCT we achieved better dissolution rates than with SO (approximately, 10 g min^{-1} vs 7.5 g min^{-1}), and more homogeneous and limp oleogels were obtained (see Fig. S.2 in supplementary data). The most highlighted characteristic of these gels was that they were odorless, principally at high EC concentrations. Additionally, their batch to batch preparation was very reproducible, regarding their mechanical and color characteristics, as well as the complete absence of EC lumps. The work of Gravelle et al. (2012) proposed that variations in the manufacturing process, EC viscosity and the addition of surfactants may have drastic effects in the mechanical properties of EC oleogels. Considering these results, perhaps the reproducibility observed in our work was mainly due to the use of lower concentrations of EC and a slow cooling.

On this basis, the flow behavior of EC solutions in MCT for four ECs with different MMW at concentrations between 4 and 23% (w/w) was explored. At concentrations below 5% (w/w) viscous solutions were

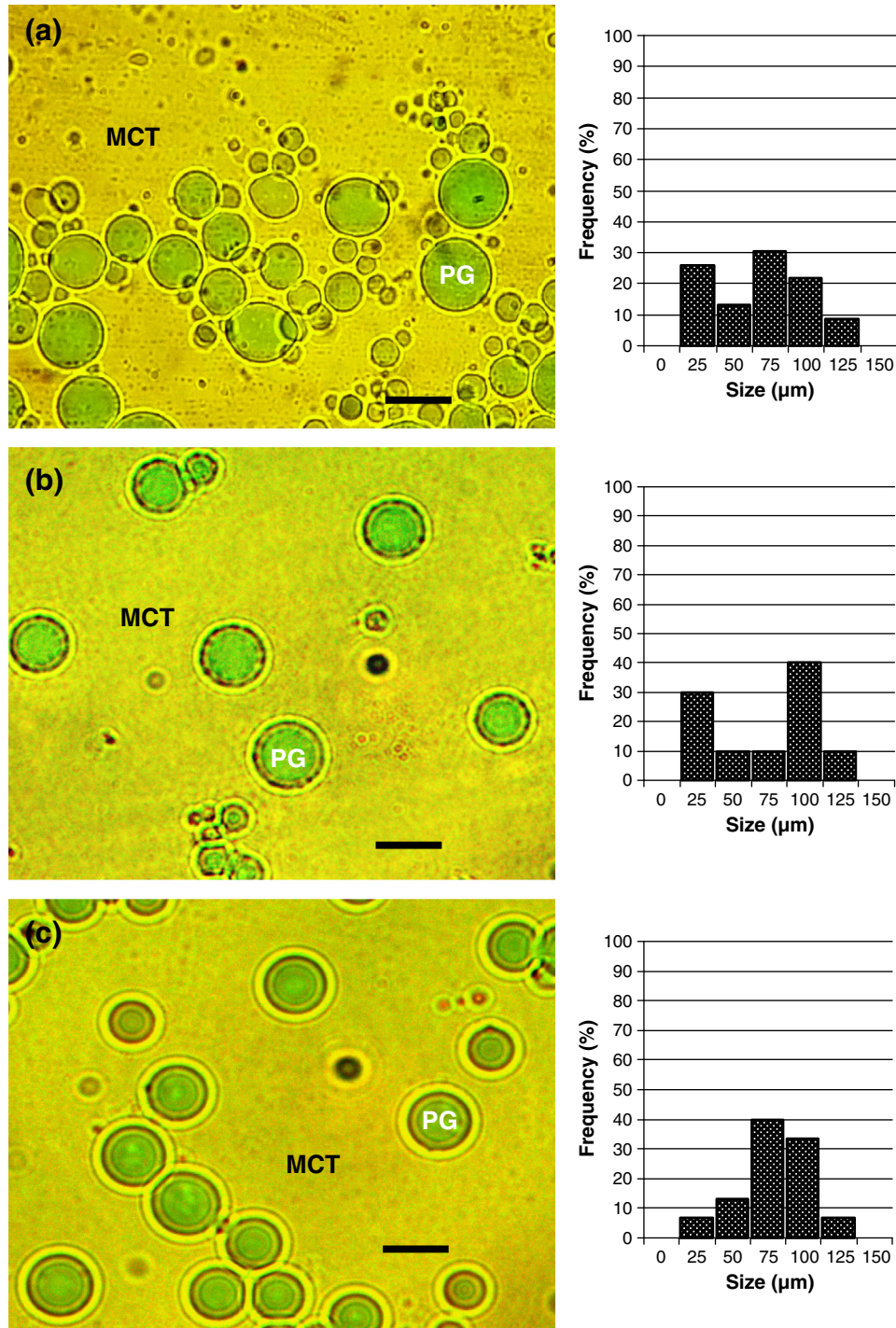


Fig. 2. Photomicrograph of freshly prepared emulsions: (a) 2:1 MCT:PG emulsion stabilized with 2% (w/w) EC-10 in the continuous phase, at 100× magnification (bar = 100 μm), (b) 1:1 SO:PG emulsion stabilized with 1% (w/w) EC-20 in the continuous phase, at 100× magnification (bar = 100 μm) and (c) 2:1 MCT:PG emulsion stabilized with 2% (w/w) EC-20 and 1% (w/w) PGPR in the continuous phase, at 100× magnification (bar = 100 μm). Samples (a) and (c) were prepared with rotor-stator homogenizer at 8000 r.p.m., and sample (b) was prepared with vortexing at 3200 r.p.m.

obtained with all ECs studied at room temperature. However, at concentrations between 5 and 7% (w/w), gelation occurred, and the resultants gels were soft and thixotropic, since their structure became totally fluid when a minimal agitation was applied. In Table 1 we present the results of apparent viscosity at 40 1/s of EC solutions in MCT. As it was expected, these solutions showed a concentration and MW dependent increase in apparent viscosity. The rheograms indicate that the samples with 4% EC show a pseudoplastic behavior giving the lower viscosity values. From 5% EC, the flow behavior shows that the solutions are Herschel–Bulkley,

because a threshold force (yield value) is required to begin flow. This is in agreement with the observation of macroscopic thixotropy in 5–7% EC oleogels at room temperature (see Fig. S.3 in supplementary data).

Effect of EC in the mechanical behavior of oleogels

At concentrations above 7% (w/w) EC induced the formation of gels, whose strength was dependent on the MMW of the polymer, oil composition and conservation status, in agreement with previous results

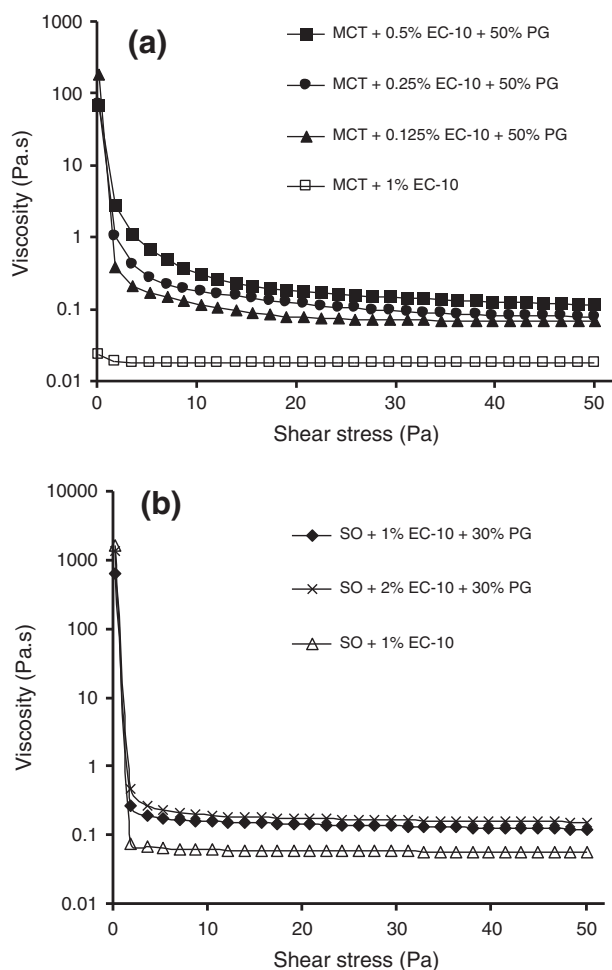


Fig. 3. Evolution of the viscosity at 25 °C for: (a) MCT with 1% EC-10 (open square) and freshly prepared 50/50 PG/MCT with 0.125% (filled triangle), 0.25% (filled circle) and 0.50% (filled square) EC-10 and (b) SO with 1% EC-10 (open triangle) and 30/70 PG/SO emulsions stabilized with 1% (filled diamond) and 2% (cross) EC-10 as a function of shear stress. In both cases, the emulsions were obtained by vortexing at 3200 r.p.m.

obtained with long chain triglycerides (Aiache et al., 1992; Gravelle et al., 2012; Zetzi et al., 2012). These gels could not be measured 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. Therefore, the structure of these samples was characterized by measuring the force at maximum penetration distance using a back extrusion test (Zetzi et al. (2012)). A typical back extrusion profile obtained with our measurement system is shown in Fig. 1(a). In accordance with Zetzi et al. (2012), the force at maximum penetration distance was used as a measurement of gel hardness, firmness or rigidity (Fig. 1(a), point B). In addition, and in accordance with the texture analyzer manufacturer's guide, we have considered the distance that the probe penetrates before the force at point A is reached (Fig. 1(a)) as an indication of gel elasticity. Fig. 1(b) summarizes the concentration dependence of the force at maximum penetration distance for MCT oleogels made of four ECs with different MMW. For comparison, SO oleogels prepared with the same polymers were also characterized (Fig. 1(c)).

It is interesting to note that, at concentrations of 6 and 7% (w/w) the force at maximum penetration distance increased upon increasing the MMW of the polymer, but with minor differences between samples. However, at 8% EC, a biphasic effect was observed with a statistically significant ($p < 0.05$) drop in penetration force for the two polymers with higher MMW (Fig. 1(b)). In order to rule out the possibility

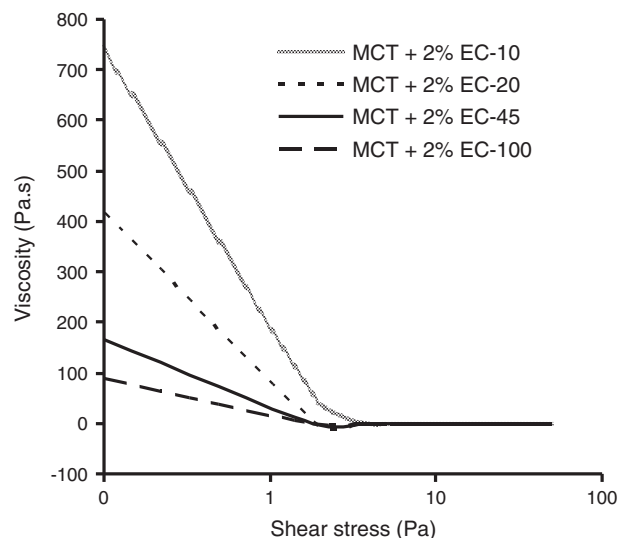


Fig. 4. Viscosity at 25 °C for freshly prepared 50/50 PG/MCT emulsions stabilized with 2% EC of varying molecular weights in the continuous phase, as a function of shear stress. All samples were obtained with vortexing at 3200 r.p.m.

that this result could be due to a longer gelation time required for the polymers with the higher MMW, we studied the time dependence of the gel structure properties, as measured by the back extrusion test. This experiment showed that the maximum strength of the gels is attained after 24 h incubation at 4 °C temperature (data not shown).

Structurally, the interactions between the tridimensional network of the gel with the liquid phase determine the mechanical behavior and stability of the system (Aiache et al., 1992; Shapiro, 2011; Smewing, 1999). In addition, as the MMW of the polymer is increased a greater number of intermolecular interactions can be formed that can potentially affect polymer–oil interactions and the overall properties of the gel (Zetzi et al., 2012). This could be one of the reasons that gels formed with 8% EC show a drop in penetration force for the two polymers with higher MMW. At 9% EC it is possible that the effect on gel elasticity and hardness overcomes any possible effect due to increased intermolecular interactions that could be present in the polymers with higher MMW. This can be seen observing the distance that probe penetrates before point A is reached in the test (Fig. 1(a) and (d)). A short penetration distance before point A is reached indicates a brittle gel whereas a large distance of penetration before rupture indicates a more elastic gel. For all four 8% EC oleogels, this distance remained fairly constant and short, suggesting that the increase in MW of the polymer is compensated by intermolecular interactions, giving rise to brittle gels with similar elasticity (Fig. 1d). In concurrence with the trend observed in penetration force, gels at 9% EC showed an increase in elasticity, with increasing MMW of EC, suggesting that at this concentration of polymer the structuring effects predominate over intermolecular interactions (Fig. 1d).

Preparation and stability of PG emulsions in MCT

Recent studies of the effect of surfactants on organogels formed by EC in SO have shown that the gel network is not only supported by intermolecular hydrogen bonding between EC molecules, but also by interaction between the hydroxyl groups of the polymer and the surfactant (Gravelle et al., 2012). We were therefore interested in exploring whether EC could stabilize a non-aqueous emulsion of PG in MCT. It is worth mentioning that upon mixing different proportions of PG with MCT or SO the emulsions were not stable in the absence of any surfactant, since the mixtures separated in two phases spontaneously within 20–30 s. Interestingly, although EC is insoluble in PG,

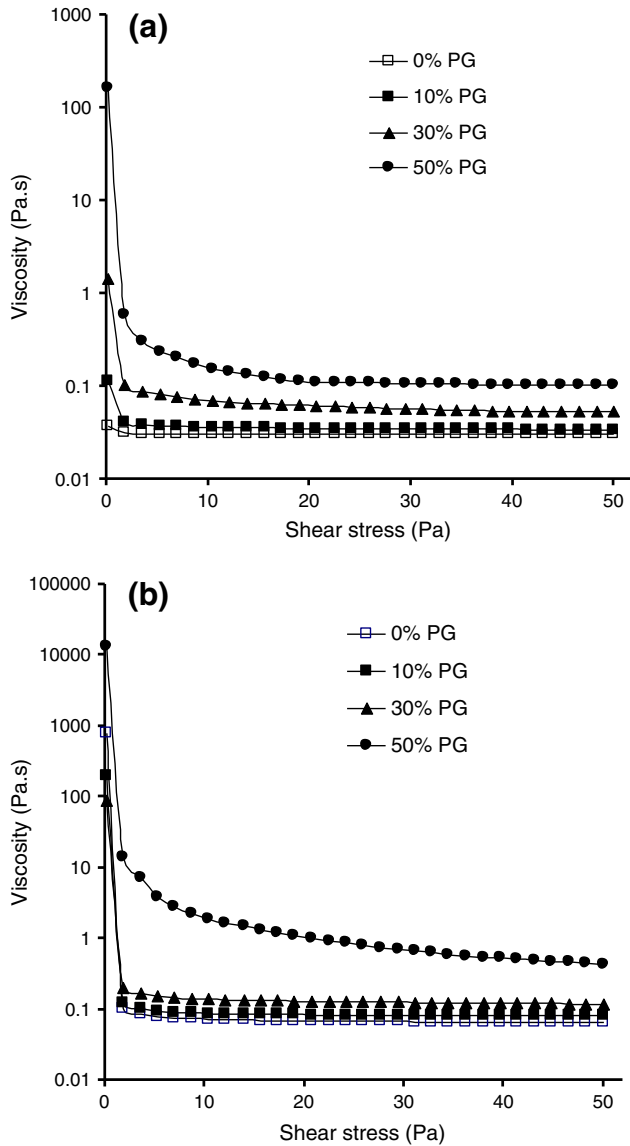


Fig. 5. Effect of PG concentration on the viscosity and yield value at 25 °C of emulsions stabilized with 2% (w/w) EC-45 in MCT (a) and SO (b): 10% PG (filled square), 30% PG (filled triangle) and 50% PG (filled circle).

cream-like emulsions were obtained at room temperature within a few seconds after PG addition to EC/oil mixtures. Although in some cases the emulsion was instantaneously formed after PG addition, force homogenization was used in order to standardize the procedure (see [Materials and methods](#) section for details). All emulsions were obtained within 10 s of applied force either using vortexing or rotor-stator homogenization.

As expected, the macroscopic appearance of the emulsion formed by PG in EC containing MCT was more homogeneous when rotor-stator homogenization (with intense shearing) was used. Curiously, the microstructure of the emulsions was similar for the oils and procedures employed for their preparation (Section 3.4).

In any case, the formation of emulsions led to structuring of the oil in such a way that they did not flow when the tube was inverted. Emulsions formed in this way were macroscopically stable for at least one month at room temperature with very little exudate. These results indicate that, independent of the mechanism by which the emulsion stabilization is produced, EC is a very effective emulsifier agent in non-aqueous emulsions. Moreover, an important aspect to note is the simplicity of their preparation, especially considering that obtaining

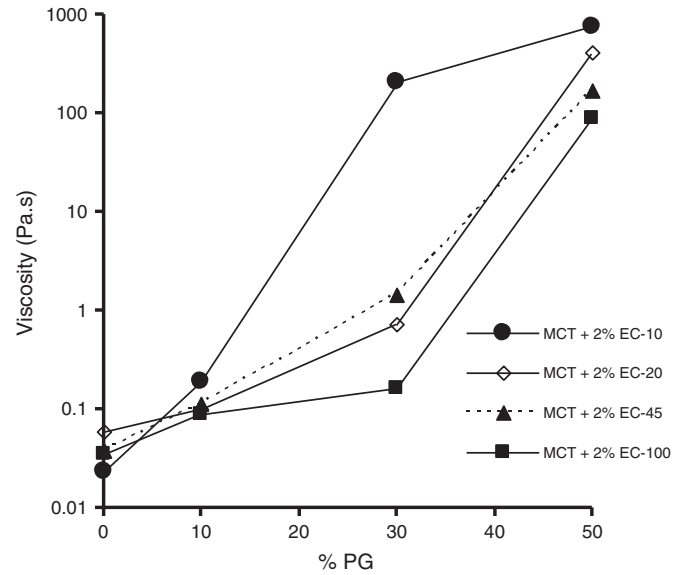


Fig. 6. Viscosity at minimal registered shear stress (0.1 Pa; 25 °C) for PG-in-MCT emulsions stabilized with 2% EC with different MMW as a function of PG concentration.

non-aqueous emulsions generally presents more technical difficulties frequently requiring the use of a special equipment for their preparation than water-based emulsions (either w/o or o/w).

Emulsion structure characterization

Optical microscopy allowed us to show that the microstructure of PG-in-oil emulsions stabilized by EC was similar for the procedures and oils employed, as well as the MMW of the polymer and its concentration (Fig. 2(a) and (b)). In addition, Fig. 2(c) shows that the emulsions formed are stable in the presence of a co-surfactant like PGPR. According to theoretical aspects of the function of tensioactive molecules, the solubility of EC in the oil phase and its insolubility in

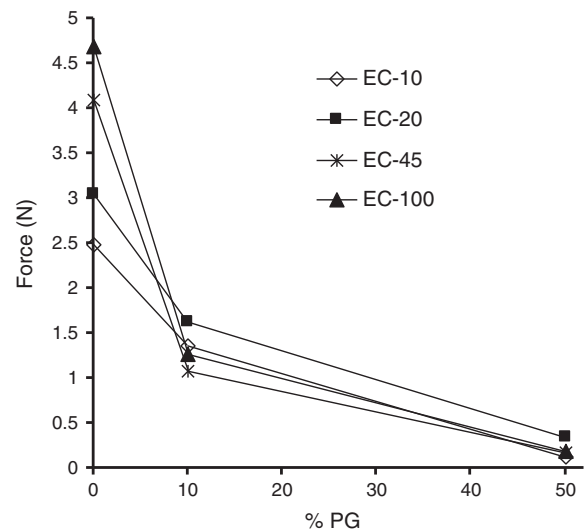


Fig. 7. Back extrusion force at maximum penetration distance (20 mm) for PG-in-MCT emulsions obtained from 7% EC oleogels as a function of PG concentration. 0% PG corresponds to starting oleogel and is included for comparison. Solid lines are simply to guide the eye.

PG under all the conditions tested (heating, shaking, co-solvent) it is reasonable to expect that a PG-in-oil emulsion should be obtained (Hasenhuettl, 2010a). Nevertheless, Meltzer et al. described that in EC-stabilized emulsions and depending on temperature, a phase inversion could occur (Melzer et al., 2003). Therefore, in order to identify the dispersed phase in our systems, the emulsions were stained with methylene blue. This polar dye is freely soluble in PG but it is totally insoluble in the tested oils. Thus, it was possible to observe that a PG-in-oil emulsion was obtained. Even though the drops were not totally uniform in size, at all PG proportions tested, spherical globules with minimal deformations were observed. Furthermore, the presence of the co-surfactant PGPR did not affect the stability of the system indicating that the emulsions formed are fairly stable (Fig. 2(c)).

Flow properties of emulsions obtained using low concentrations of EC

Considering that at concentrations below 5% (w/w) EC solutions in MCT or SO and the respective PG-in-oil emulsions are viscous and fluid, the measurement of their flow properties was chosen for their characterization.

Effect of EC concentration and MMW

As it is observed in Fig. 3(a), EC solutions in MCT behave as classical Newtonian fluids. When 50% (w/w) PG was added to MCT containing different concentrations of EC, the emulsions obtained had totally different flow properties. This could be seen at low shear stress with the appearance of a sharp yield value typical of a pseudoplastic fluid. This behavior was similar to 10% and 30% (w/w) PG emulsions (data not shown). As we expected, rising EC concentration caused a displacement of the isotherms towards higher apparent viscosity values.

When we used SO instead of MCT, the general trend of fluid properties was similar except that the behavior was pseudoplastic even in the absence of PG (Fig. 3(b)). It is interesting to note that the flow properties of PG emulsions in MCT were more sensitive to the addition of very low concentrations of EC than those formed in SO.

Perhaps the most unexpected finding of PG emulsions in MCT was the independence of the observed effects with the MMW of the EC used at high shear stress, while an inversely proportional effect at low shear stress was observed (Fig. 4), taking into account that for most of the polymers studied so far it is generally observed that their addition to a solution induces a greater increase in viscosity as the MMW is increased. In this context, it has been suggested that the stabilizing effect of polymers on emulsions might be due to an increase in viscosity of the continuous phase (kinetic effect). The independence on the MMW of the polymer, or even an inverse dependence, could suggest that one component in the stabilization of PG-in-oil emulsions by EC is the presence of the polymer in the interface.

Dependence of emulsion flow properties on the proportion of PG

As stated above, the incorporation of PG into MCT or SO containing EC led to the formation of emulsions of PG in a continuous oil phase. Interestingly, an important increase in viscosity and pseudoplastic behavior of the emulsions was observed upon increasing the proportion of PG (Fig. 5(a)). In Fig. 5(a), the flow curve for 2% (w/w) EC-45 in MCT is shown as an example. A similar trend was observed for the other ECs with different MMW (data not shown).

When the emulsions were prepared using SO as the oil phase, the increment in apparent viscosity and yield value was lower than in MCT with 10 and 30% (w/w) PG. However, a significant increase in emulsion apparent viscosity was observed upon addition of 50% (w/w) PG (Fig. 5(b)).

Somehow counter-intuitively, the emulsions formed using MCT as the oil phase, displayed higher viscosities when they were stabilized using ECs of the lower MMW (Fig. 6). These results support the above interpretation that the stabilizing effect of EC is not due to an increase

in viscosity of the continuous phase but rather to the surface activity of the polymer.

Emulsions obtained from high concentrations of EC solutions and back extrusion measurements

As noted above, when the concentration of EC in MCT was between 5 and 7% (w/w), gelation occurred; the resultant gels were soft and some of them were thixotropic, because their rigid structures became totally fluid when a minimal stress was applied. Therefore, a back extrusion test was used to characterize the structural properties of these emulsions. Contrary to what was observed at low concentrations of EC, a dramatic de-structuring effect was observed upon the formation of PG emulsions using these solutions of EC in MCT (Fig. 7). This result is probably due to the interruption of the gel network by liquid droplets of PG.

Conclusions

In conclusion, our results disclose a novel EC stabilized non-aqueous PG-in-oil emulsion system.

In summary, the results described herein show that:

- EC is readily soluble in MCT forming viscous solutions below 5% (w/w) and oleogels above 7% (w/w);
- EC dissolved in medium chain triglycerides (MCT) or soy oil (SO) can stabilize non-aqueous microemulsions of propylene glycol (PG) as a dispersed phase without the requirement of co-surfactants. The emulsions thus formed are easily obtained and show a very good macroscopic stability for at least one month at room temperature.
- The effects of EC on the flow properties of the PG-in-oil emulsions are independent of the MMW of the polymer suggesting that the polymer is stabilizing the emulsions by its surface activity rather than by an increase in viscosity of the oil phase.

Altogether, the physico-chemical properties and the good biocompatibility of the system open the possibility of using this platform for the design of novel fat reduced foods as well as for the substitution of long chain saturated triacylglycerols for healthier oils. Further studies are in progress to evaluate the potential of using these emulsions to incorporate and stabilize active ingredients with different polarities.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.foodres.2014.03.040>.

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