



Structural and mechanical properties of organogels: Role of oil and gelator molecular structure



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ABSTRACT

This work aims at evaluating the influence of oil and gelator structure on organogels' properties through rheological measurements, polarized microscopy and small-angle X-ray scattering (SAXS). Four different food-grade gelators (glyceryl tristearate – GT; sorbitan tristearate – ST; sorbitan monostearate – SM and glyceryl monostearate – GM) were tested in medium-chain triglyceride and high oleic sunflower (MCT and LCT, respectively) oil phases. Organogels were prepared by mixing the oil phase and gelator at different concentrations (5, 10, 15, 20 and 25%) at 80 °C during 30 min. All organogels presented birefringence confirming the formation of a crystalline structure that changed with the increase of the gelator concentration. Through the evaluation of SAXS peaks it has been confirmed that all structures were organized as lamellas but with different *d*-spacing values. These particularities at micro- and nanoscale level lead to differences in rheological properties of organogels. Results showed that the oil type (i.e. medium- and long-chain triglyceride) and hydrophilic head of gelators (i.e. sorbitan versus glyceryl) exert influence on the organogels physical properties, but the presence of monostearate leads to the formation of stronger organogels. Moreover, gels produced with LCT were stronger and gelled at lower organogelator concentration than MCT.

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1. Introduction

Edible organogels, or oleogels, have recently generated an enormous interest for scientific and technological reasons in several fields including cosmetic, pharmaceutical and food science. In foods, edible oleogels have also called the attention due to their unique properties that allow shaping foods in terms of e.g. texture and appearance, while also allowing the introduction of e.g. bioactive or functional compounds. Additionally, the emerging of organogels are related with: a) the thermoreversibility between solid and liquid by heating above and cooling below the transition temperature, which changes according to physicochemical properties of the gelator and the continuous phase (Abraham et al., 2012; Toro-Vazquez et al., 2013); and b) the potential health benefits that they may bring if used as alternative ingredient in foods containing saturated and/or trans fatty acids, as they have shown the capacity to provide texture to food products (Rogers, Wright, & Marangoni, 2009).

Organogels can be formed by the self-assembly of surfactant molecules (organogelators) into three-dimensional networks that entrap an organic liquid through capillary forces (Terech & Weiss, 1997). They can be produced due to physical forces and chemical interactions depending on the kind of gelator used: polymeric or low molecular weight organogelators (LMOGs) (Vintiloiu & Leroux, 2008) with molecular weight lower than 3000 Da (Abdallah & Weiss, 2000). Gelator structure exerts a great influence on organogel properties since the ability to form supramolecular gels is only possible with very specific materials. The gelling ability is related to the balance between the soluble and insoluble fractions of the gelator in the solvent. The molecule must be relatively insoluble to self-assemble into anisotropic structures. On the other hand, it must have a soluble fraction to interact with the oil moieties (Co & Marangoni, 2012). Despite the recently published studies using different gelators on organogels development (Davidovich-Pinhas, Barbut, & Marangoni, 2016; Martins, Cerqueira, Fasolin, Cunha, & Vicente, 2016; Valoppi et al., 2017), it is still of great interest to explore how the chemical structure of the gelator influences organogel formation at molecular level. The relationship between the structures, their structural specific characteristics and rheological properties is of utmost interest aiming their use in

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technological applications. In addition, the oil phase properties (e.g. triglycerides' carbon chains size and degree of saturation) change the way in which gelators generate a three-dimensional network (Gravelle, Davidovich-Pinhas, Zetzl, Barbut, & Marangoni, 2016) and must be studied. Recently, the development of organogels using food grade materials has been increasing due to their possible applications in food and pharmaceutical products. Organogels using ethyl cellulose (Davidovich-Pinhas, Barbut, & Marangoni, 2015a; Gravelle et al., 2016), waxes (Martins et al., 2016; Toro-Vazquez, Alonzo-Macias, Dibildox-Alvarado, & Charo-Alonso, 2009; Yilmaz & Ogutcu, 2014), monoglycerides (Chen & Terentjev, 2009; Co & Marangoni, 2012; Lopez-Martinez, Charo-Alonso, Marangoni, & Toro-Vazquez, 2015; Lopez-Martinez et al., 2014; Valoppi et al., 2017) and sorbitans (Murdan, Gregoriadis, & Florence, 1999; Perneti, van Malsen, Kalnin, & Floter, 2007; Sanchez, Franco, Delgado, Valencia, & Gallegos, 2011) are some of the materials that have been used to gel edible oils.

Sorbitan esters, also called spans, are non-ionic surfactants, which are hydrophobic in nature and that can act as emulsifiers and structuring agents in organic solvents. In particular, Span 60 and Span 65 are esters of sorbitan and stearic acid, differing by the number of alkyl chains (esterification degree) and presenting one and three tails, respectively. In the last decade some studies reported their ability to produce organogels with edible oils, their application as fat replacer and mainly as delivery systems (Barbut, Wood, & Marangoni, 2016; Kamble, Udapurkar, Nakhat, Yeole, & Biyani, 2011; Singh, Pramanik, Ray, & Pal, 2015). Glycerol monostearate (GM) and tristearate (GT) are esterification products of glycerin and stearic acid that also differ by the presence of one and three alkyl chains, respectively. A number of studies report the use of GM to produce organogels. On the other hand, GT is usually combined with other organogelator since it is not classified as an amphiphilic molecule due the complete esterification of its hydrophilic head. Despite of this GT could be used as a potential gelator of organic solvents due its hardening properties (Sahri & Idris, 2010). Therefore, the main contribution of the present work is the improvement in the knowledge about the mechanism of organogel structure formation with food-grade ingredients, their structural and mechanical properties, since there are few works trying to unravel, explain and compare the formation mechanism of organogels with these

organogelators. Our work evaluates the effect of gelators with different hydrophilic heads (glyceryl and sorbitan group) and hydrophobic tails (mono- or tri-stearic chains) and the size of oils' carbon chain (i.e. C8–C10 or C16–18) on organogel properties. The developed organogels were evaluated by oscillatory rheology in order to understand how the molecular organization influences their mechanical behavior. These properties were correlated with their crystalline structures, which were studied through small-angle X-ray scattering (SAXS) and polarized microscopy.

2. Materials and methods

2.1. Raw materials

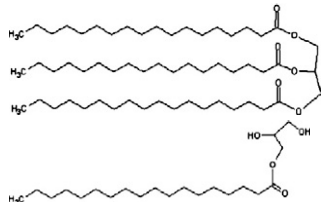
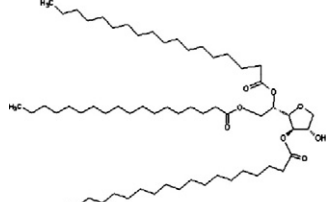
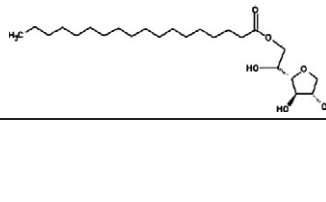

Glycerol tristearate (GT) (>98.0%), sorbitan tristearate (ST) and sorbitan monostearate (SM) of technical grade were purchased from Sigma Aldrich Chemical Co. Ltd. (USA) and glycerol monostearate (GM) (>95.0%) was obtained from Alfa Aesar (USA). Medium-chain triglycerides (MCT, Neobee 1053; composed by 55% of C8 and 44% of C10 fatty acids) was kindly supplied by Stepan Lipid Nutrition (USA) and high-oleic sunflower oil (LCT, 0.1% of C14:0, 3.8% of C16:0, 3.3% of C18:0, 80.1% of C18:1, 10.7 of C18:2, 0.3% of C18:3, 0.4% of C20:0 and 0.1% of C20:1) was donated by Cargill (Brazil). Table 1 presents the structure, hydrophilic-lipophilic balance (HLB), melting point and molecular weight of the gelators used.

2.2. Organogels production

Organogels were prepared in 8 cm height × 2 cm diameter tubes with screw caps by heating the mixture of oil phase (MCT or LCT) and the gelator (5, 10, 15, 20 and 25% w/w) at 80 °C during 30 min under magnetic stirring. Afterwards samples were allowed to cool down at 25 °C under quiescent conditions. The concentrations were chosen based on the critical gelation concentration for the gelators and the type of oil phases used (Table 1S). Gelator concentration above 15% (w/w) (upper limit to be considered as an organogel) was evaluated to help understand the interactions between components and network formation. The samples were stored at 25 ± 2 °C at least during 24 h before being analyzed. Organogels produced with MCT and LCT will be called OMCT and OLCT, respectively.

Table 1

Hydrophilic-lipophilic balance (HLB), melting point, molecular weight values and chemical structure of the gelators used for organogels production.

Organogelator	HLB	Melting point ^a (°C)	Molecular weight ^a (Da)	Chemical structure
Glycerol tristearate (GT)	2.0	55	891.5	
Glycerol monostearate (GM)	3.8	58–59	358.57	
Sorbitan tristearate (ST)	2.1	53	963.54	
Sorbitan monostearate (SM)	4.7	54–57	430.62	

^a Values obtained from suppliers and Hepworth (2006).

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