



Organogelation of extra virgin olive oil with fatty alcohols, glyceryl stearate and their mixture



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ABSTRACT

The final properties of organogels based on a mixture of gelators can be tuned by taking advantage of interactions between gelators. In this work, extra virgin olive oil was structured using glyceryl stearate (GS), policosanol (P) and their mixtures aiming at investigating their effects on the rheological properties and microstructure of obtained gels. Rheological tests evidenced that P yields a more consistent material with higher crystallization and gelation temperatures with respect to GS. Gels based on a mixture of gelators exhibit intermediate properties between those of “pure” gels, even though closer to those of P organogels. The crystallization and gelation phenomena in mixed gels seem to be dependent only on policosanol fraction, whereas dynamic moduli are affected by both gelators. Intermolecular interactions were investigated with FT-IR finding that GS is able to give hydrogen bonding whereas P works mainly through the formation of van der Waals interactions. Mixed gels exhibit a behavior close to that of P gels, even though van der Waals interactions seem less evident than in pure P gels. As a consequence, from a macroscopic point of view, the use of the mixture yields a weaker gel than that obtained with the same concentration of pure P.

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1. Introduction

Organogels (or oleogels) are solid-like materials structured in an organic solvent thanks to the self-assembly of structurant molecules (organogelators) which build a three-dimensional network. Different organogelators, mostly Low Molecular Weight (LMWO), are currently used to give stiffness to liquid solvents, in particular for foods, owing to the growing necessity to obtain healthy *trans-free* hard fats or shortenings without chemical modifications (Patel & Dewettinck, 2016). Among the LMWOs, Monoacylglycerols (MAGs) are widely investigated (Co & Marangoni, 2012), because they are very used in foodstuffs or cosmetics as emulsifiers and they are cheap and versatile. MAGs were used, for example for structuring cod liver oil aiming at analyzing the potential effect of these organogels on oxidative stability of the solvent (Da Pieve, Calligaris,

Panozzo, Arrighetti, & Nicoli, 2011). The same gelators were also investigated by Ojijo et al. (Ojijo, Neeman, Eger, & Shimoni, 2004), Lopez-Martinez et al., (Lopez-Martinez et al., 2014; Lopez-Martinez, Charo-Alonso, Marangoni, & Toro-Vazquez, 2015) and by Lupi et al. (Lupi, Gabriele, de Cindio, Sánchez, & Gallegos, 2011; Lupi, Gabriele, & de Cindio, 2012; Lupi, Gabriele, Facciolo et al., 2012).

Among other potential edible gelators, special attention was paid to waxes (Rice bran wax, candelilla wax and carnauba wax), fatty alcohols, fatty acids, sterols and sorbitan monostearate (Bot et al., 2011; Moschakis, Panagiotopoulou, & Katsanidis, 2016). In particular, fatty alcohols can be used alone to structure oil (Lupi et al., 2013), or in mixture with other components, throughout the addition of waxes extracted from vegetable sources. For example, candelilla wax is a mixture of fatty alcohols with sterols, high-melting alkanes, fatty acids and waxy esters (Mert & Demirkesen, 2016; Toro-Vazquez et al., 2013).

Recently, the effect of mixtures of gelators of different chemical nature on the rheological properties of gels has been studied, mostly aiming at tuning the final characteristics of either organogels or emulsions in which these gels are the oil phase. Quite often,

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the investigated mixtures contain MAGs, owing to the already described characteristics.

Alfutimie et al. (Alfutimie, Curtis, & Tiddy, 2014), employing different techniques, studied the phase behavior of mixed saturated and unsaturated monoglycerides (glyceryl oleate and glyceryl stearate) to investigate whether gel phases could be formed from unsaturated monoglycerides. The authors found that there was incorporation of the saturated alkyl chains into the α -gel phase formed by the unsaturated alkyl chains of the other monoglyceride and, therefore, an interaction between gelators.

Lopez-Martinez et al. (Lopez-Martinez et al., 2015) investigated organogels prepared with different amounts of MAGs with and without ethylcellulose (EC). According to the results, the addition of EC to MAGs-canola oil organogels, gave materials with higher G^* and lower oil lost during storage than those observed without EC. The authors concluded that there is a synergistic interaction between these components.

Toro-Vazquez et al. (Toro-Vazquez et al., 2013) investigated organogelled emulsions whose oil phase was structured with a mixture of candelilla wax and monoglycerides. Thanks to DSC, NMR (for Solid Fat Content measurement) and texture measurement, the authors found that the presence of MAGs affected the inter-crystal interactions in both the organogels and the emulsions, and that this phenomenon became more significant with the increase of MAGs concentration.

Starting from these considerations, the present paper aims at investigating the rheological properties and the microstructural interactions of olive oil organogels structured with Glyceryl Stearate (GS), fatty alcohols (P) and mixtures of them.

GS is interesting because it is widely used in different areas (foods, cosmetics) and is based on stearic acid, a saturated fatty acid that is considered “neutral” for cholesterol and cardiovascular issues (Marangoni, 2009). On the other hand, P was recently proposed as an organogelator, whereas in the past, it was mainly known as food supplement owing to its positive effects on cholesterol and cardiovascular diseases (Xu, Fitz, Riediger, & Moghadasian, 2007). Even though more expensive than GS, it seems very effective in edible oil gelation, as a consequence, it can be interesting to investigate the properties of the mixture of this MAG and these fatty alcohols with respect to the effects of single gelators.

The rheological investigation of edible LMW organogels is nowadays diffusely available in the literature, but a microstructural characterization based on the intermolecular interaction between gelators analyzed with FTIR spectra, and focused on organogels made with extremely impure solvents like commercial edible oils, is still not deeply investigated. Therefore, the paper aims at giving a deep explanation on the rheological properties of these complex systems related to the weak interactions typical of LMW organogels.

2. Materials and methods

2.1. Materials and samples preparation

Organogels were prepared with an extra virgin olive oil (EVO), supplied by Gabro (Italy), as the solvent and tocopherol as an antioxidant; the adopted organogelators were policosanol (P) from rice bran wax (Lupi et al., 2013), glyceryl stearate (GS) and their mixtures. All the ingredients were supplied by A.C.E.F. (Italy).

Organogels were produced by adding tocopherol in the extra virgin olive oil to prevent oxidation (the ratio tocopherol/olive oil was kept constant and equal to $6.15 \cdot 10^{-4}$ (w/w) (Lupi, Shakeel et al., 2016)), and then heating the oil in a water bath thermostated by a plate heater (VELP Scientific, Italy) up to 85 °C.

Afterwards, the gelator (i.e. P or GS or a mixture of both) was added to the hot oil, and the system was continuously stirred (stirrer RW 20, IKA-Werke, Germany). On complete melting of organogelator, mixing was continued for at least 5 min before starting the rheological study.

Organogels produced with GS are indicated as ‘OG’ samples within the text, P organogels are called ‘OP’ samples, and, finally, systems made by mixing the two organogelators are indicated as ‘OM’ samples. Samples are labeled with a subscript indicating the total amount of gelator added to the oil (see Table 1).

2.2. Rheological characterization

Organogels (except for samples OG_{0.02} and OP_{0.02}, analyzed only with FTIR tests) were investigated with a controlled stress rheometer (DSR500, Rheometric Scientific, USA, parallel plates 40 mm, gap 1.0 ± 0.2 mm) where temperature is controlled by a Peltier system.

Preliminary amplitude sweep tests were carried out at different constant temperatures from the preparation value, i.e. 85 °C, down to 20 °C almost every 10 °C to examine the potential changes in the linear viscoelastic region.

Temperature ramp tests (time cure) were, then, performed at constant frequency of 1 Hz and in the linear viscoelastic regime by cooling the sample from 85 °C down to 20 °C (or down to 10 °C for OG samples) with a cooling rate of -1 °C/min. All samples were independently prepared three times and experimental results are shown in terms of average value and standard deviation, typically lower than 10%. Larger deviations were seldom observed either for data at high temperature, owing to instrument limits, or for data in the transition crystallization region, owing to the fast structuring phenomena.

The onset of crystallization (T_{co}) was defined as the temperature value at which an abrupt increase of complex modulus G^* (and a rapid decrease of the loss tangent curve) in temperature ramp tests is observed (Lupi et al., 2012; Lupi et al., 2013).

The temperature at which clusters of crystals start to interconnect in a network structure, can be considered as the gelation temperature (T_g). Even though the rigorous determination of the gel point should be carried out according to the well-known Winter's theory (Chambon & Winter, 1987), more approximate criteria are used often for a faster estimate of a transition temperature. Among the different proposed criteria, the crossover between dynamic moduli is often used even if, being frequency dependent, it is not the real gel point (Chambon & Winter, 1987; Curcio et al., 2001; Rao, 1999). Starting from these considerations, in the present work, for simplicity, the gelation temperature was estimated as the crossover between dynamic moduli i.e. the temperature at which the loss tangent is equal to unity and, therefore, the phase angle (δ) is 45° (Lupi et al., 2012).

Experimental data of storage modulus, G' , were fitted as a function of the organogelator fraction, according to a fractal model already used in the literature to describe fat crystal networks (Tang & Marangoni, 2007) and recently adopted also to analyze organogel behavior

$$G' = \lambda \cdot X_0^{\frac{1}{3-D}} \quad (1)$$

The storage modulus is usually related to the fat crystal volume fraction (Tang & Marangoni, 2007). Nevertheless, the mass fraction of organogelator being easier to measure and proportional to the crystal volume fraction (Lupi et al., 2013), it was chosen to fit G' as a function of the organogelator fraction X_0 . In Eq. (1), λ is a constant determined by the links between fat crystal flocs, and D is the fractal dimension. A linearized form of Eq. (1) is shown in Eq. (2)

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