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Regular Article

The effects of intermolecular interactions on the physical properties of organogels in edible oils

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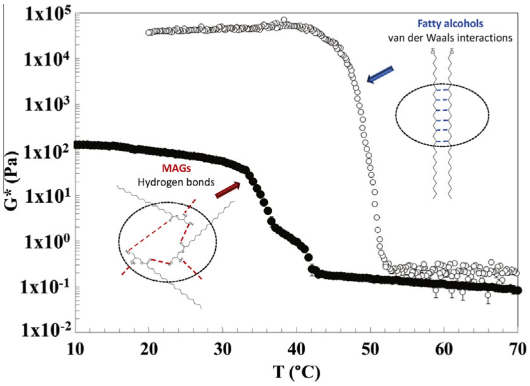
GRAPHICAL ABSTRACT



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ABSTRACT

The microstructure of organogels based on monoglycerides of fatty acids (MAGs) and policosanol and on different edible oils was investigated by using different techniques (calorimetry, nuclear magnetic resonance, infrared spectroscopy, rheology, polarized light microscopy) towards a better understanding and control of the oil gelation phenomena. Dynamic moduli were related via a fractal model to microstructural information such as solid content and fractal dimension. Infrared spectroscopy evidenced that network structure in MAGs gel is mainly due to hydrogen bonding, whereas in policosanol system is mainly given by van der Waals interactions. Because of the different relative contribution of molecular interactions, the investigated organogelators exhibit a distinguished macroscopic behavior. MAGs are sensitive to the utilized oil and structuration occurs quickly, even though at a temperature lower than policosanol. Policosanol organogels exhibit a behavior independent of the used oil and a slower gelation rate, as a result of the weaker van der Waals interactions. Nevertheless, at lower concentration a stronger final gel is obtained, probably due to of the large number of interactions arising among the long alkyl chains of the fatty alcohols. Obtained results evidenced that policosanol is very effective in gelation of different oils and seems promising for potential commercial uses.

1. Introduction

Organogels or oleogels are innovative materials considered as valuable substitutes for reducing saturated or *trans* fats in food industry [1–3] as well as rheological modifiers in cosmetical or

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pharmaceutical formulations [4]. In food applications, edible oil organogels are one of the most promising alternatives for designing new hardstocks without the addition of hydrogenated or saturated fats. A wide body of literature reports on the use of different organogels in food materials: Zetzl et al. [5] used ethylcellulose gels for substituting saturated fats in frankfurters, Lupi et al. used monoglycerides of fatty acids (MAGs), fatty alcohols or soy lecithin for structuring meat sauces [6,7], Toro-Vazquez et al. [8] described the use of MAGs and waxes oleogels for hardening water-in-oil food emulsions. Various other food applications of different organogels were reviewed by Co and Marangoni [3], Wang et al. [9], and Patel and Dewettinck [10]. In cosmetical or pharmaceutical applications organogels are mainly used as carriers for controlled drug delivery in oral [11,12] or topical [13–15] uses because of their ability to dissolve lipophilic components and to release them with a controlled rate depending on the organogel's rheological properties.

Organogels can be categorized by the carbon chain length of the used organogelators. Organogelators can be divided into LMWO (low molecular weight, up to C_{36} [16]) or PO (polymeric, with longer chains). In food applications, LMWOs are more commonly used than POs, due to their ability to provide structure to vegetable oils and for being edible. Even though these systems are investigated from rheological, chemical, physical, and microstructural point of view, knowledge about the gelation mechanism is still missing. It seems evident that the network structure is based on noncovalent forces such as van der Waals interactions, dipole-dipole interactions [17–20], and predominantly by hydrogen bonding (H-bonding) [18,21]. According to the different interaction potential, organogelators are usually classified between hydrogen-bond-based and nonhydrogen-bond-based compounds [20].

Monoglycerides of fatty acids (MAGs) are a typical example of edible hydrogen-bond-based gelators [22] and they are among the rare systems capable of self-assembling both in aqueous and organic media [23,24]. Aqueous solutions of MAG form different liquid crystalline mesophases upon cooling and in ternary MAG/oil/water systems, the presence of water usually dominates the behavior of structuring MAG [25,26]. On the contrary, the phase behavior of MAG in hydrophobic solvents in less studied. Da Pieve et al. [27] analyzed MAG/cod liver oil gels using a polarizing light microscope and showed a needle-like morphology of MAG crystals. Kesselman and Shimoni [28] confirmed this result for MAG/olive oil gels and reported the formation of additional spherulitic or rosette-like microstructure using corn oil as the solvent. It is suggested that the oil influences the microstructural features of MAG crystals or as reported by Co and Marangoni [3] the differences in MAG crystal morphology may be also attributed to the presence of impurities in the oil. From a rheological point of view, several papers are available on MAGs behavior describing both oscillation [3,29–31] and shear properties [32].

In recent years, several other organogelators were studied to gel edible oils, mainly based on waxes, fatty alcohols [11,29,33,34], and their mixtures with other gelators [8,35]. For example, Schaink et al. [36] investigated the gelling capabilities of a mixture of stearic acid and stearic alcohol in sunflower oil. Gandolfo et al. [37] studied the oil-structuring potential of fatty acids, fatty alcohols and their mixture in sunflower, soybean, and rapeseed oil. The authors observed also the synergistic effect given by mixtures of gelators with the same chain lengths. Lupi et al. [29] investigated the potential structuring effect of policosanol, a mixture of fatty alcohols in which the major component is octacosanol in olive oil. The same authors investigated policosanol organogels to produce carriers for ferulic acid delivery by ingestion [11]. This gelator seems particularly promising because it is already used as dietary supplement and is able to gel edible oils in relatively small amounts [29].

The present paper reports on the self-assembly of MAGs and policosanol organogels with different techniques such as rheology, infra-red spectroscopy (FT-IR), DSC (differential scanning calorimetry), NMR (nuclear magnetic resonance), and polarized light microscopy with a rheo-optical system. Although MAGs are widely used and studied, a systematic and comprehensive investigation of their properties and microstructure is still missing. Policosanol was only recently investigated and detailed information on gelation phenomena and intermolecular interactions is not yet available. The comparison of policosanol to better known gelators such as MAGs, aims towards a more generic understanding of the gelling behavior and the resulting microstructure and rheology of organogels. The effect of different edible oils was investigated to evaluate potential differences in gelation phenomena depending on solvent-gelator interactions.

2. Materials and methods

2.1. Materials and samples preparation

Organogels were produced with commercial virgin olive oil ('V', De Santis, Italy), extra-virgin olive ('E', Gabro, Italy), and sunflower oil ('S', De Santis, Italy). As first organogelator, a commercial MAG ('M') as a mixture of monoglycerides of fatty acids with an equal mass fraction of monopalmitin and monostearin (Myverol 18-04K, Kerry Group, Ireland) was used. As second organogelator, policosanol ('P') from rice bran wax (composed of 60%w/w octacosanol [29], A.C.E.F., Italy) was utilized. Sample notation indicates the oil and organogelator along with the concentration X of the respected organogelator. For example $VM_{0.03}$ would be a virgin olive oil gelled with 0.03 weight fraction of MAG. All samples were prepared in a water bath thermostated by a plate heater (Jolly 2, Falc Instruments, Italy) adding the organogelator to the oil previously heated up to 70 °C for MAG-gelled samples and 85 °C for VP samples. The system was continuously stirred using a laboratory mixer (RW 20, IKA, Germany) and maintained at the temperature of preparation until tests were performed. Investigated samples are reported in Table 1.

2.2. Rheological measurement

2.2.1. Oscillatory and shear rheology

VM samples were analyzed with a controlled strain rheometer ARES-RFS (TA Instruments, USA) equipped with a parallel plate geometry (diameter = 50 mm, gap = 1 ± 0.1 mm) whereas VP samples were studied with a DSR-200 (Rheometric Scientific, U.S.A.) equipped with a parallel plate geometry (diameter = 40 mm, gap = 1 ± 0.1 mm). Organogels are highly temperature-dependent materials and, therefore, the temperature of the lower plate was carefully controlled by a Peltier system (±0.1 °C). Temperature ramp tests (time cure) were performed in linear viscoelastic regime from 70 °C to 10 °C in the case of VM samples and from 85 °C to 20 °C for VP samples applying a cooling rate of -1 °C/min [29,30]. Lower final temperatures (down to 0 °C) were applied to samples exhibiting a low onset of crystallization (lower than 10 °C). Two parameters, T_{co} and T_g, were estimated from the analysis of the obtained temperature ramp tests. The onset of crystallization temperature (T_{co}) was calculated following the procedure described by Lupi et al. [30], as the temperature at which a strong increase of the complex modulus G^* and, thus, a sudden decrease of loss tangent was observed. The gelation point (T_g) was identified as the crossover of both dynamic moduli, i.e. where the loss tangent is equal to unity [29,30]. Considering that, for samples having a gelator fraction greater than a threshold, these two parameters can be nearly equal, differences among them were analyzed using *t*-student test (Statgraphics Centurion XV, USA). They were