



Rheological properties of organogels developed by sitosterol and lecithin



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ABSTRACT

Mixtures of sitosterol (S) and lecithin (L) are able to prepare food-grade organogel by structuring liquid edible oil. In this paper, various S to L mass ratios (i.e., S0L10 to S10L0) in the sunflower oil (SO) high in trillinolein were used to develop organogels at three storage temperatures (T_s : 5, 15 and 25 °C). Influences of mass ratio and storage temperature on the rheological properties of organogels after ten days of storage were evaluated in detail, and the corresponding microstructures of the crystal network in these organogels were studied by microscopy. At each storage temperature, the rheological properties of the organogels formed by sitosterol and lecithin were different from organogels formed from sitosterol alone. The crystal microstructure in organogels also revealed a dependence on structurant composition and T_s . By increasing T_s , the elasticity and thermal stability of the organogel developed by mixed structurant were enhanced, and the length of microplatelet units was increased along with a decrease in mesh size, leading to the formation of higher ordered networks, and therefore, the most typical example (S8L2 organogel at $T_s = 25$ °C) had a higher elasticity than other organogels. The observed rheological behavior is likely to be associated with the composition of structurant, the storage temperature, the viscosity of liquid oil and the microstructure of crystal network.

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1. Introduction

The diversity of the microscopic and mesoscopic structures of low molecular weight organogels makes them interesting soft materials with numerous theoretical and practical applications (Behera, Sagiri, Pal, & Srivastava, 2012; Lupi et al., 2012; Terech & Weiss, 1997). The potential of these organogels as an alternative liquid oil structuring technique has become an active area of research in the past decade, mainly due to pressures to reduce saturated fat intake and to eliminate *trans* fats from our diets (Co & Marangoni, 2012; Dassanayake, Kodali, & Ueno, 2011). Many types of low molecular weight organogelators including monoacylglycerides (Da Pieve, Calligaris, Panozzo, Arrighetti, & Nicoli, 2011; Goldstein & Seetharaman, 2011), vegetable waxes (Hwang, Kim, Singh, Winkler-Moser, & Liu, 2012), ceramides (Rogers, Wright, & Marangoni, 2009), hydroxylated fatty acids (e.g., ricinoleic acid and 12-hydroxystearic acid) (Rogers, Wright, & Marangoni, 2008; Wright & Marangoni, 2007) and fatty alcohols (Lupi et al., 2012) have been reported to be successful in making organogels from edible oil. Recently, the polymer ethyl cellulose was reported to form a polymer gel in triacylglyceride (TAG) oils (Gravelle, Barbut, & Marangoni, 2012; Laredo, Barbut, & Marangoni, 2011; Zetzl, Marangoni, &

Barbut, 2012). In most cases, the physical properties from the development of mixed self-assembled structures outperform the pure components (Pernetti, Van Malssen, Flöter & Bot, 2007). Examples of such structurant mixtures are γ -oryzanol + β -sitosterol (Bot & Agterof, 2006; Bot, den Adel, & Roijers, 2008; Bot et al., 2011), fatty acid + fatty alcohol (Schaink, Van Malssen, Morgado-Alves, Kalnin, & Van der Linden, 2007), lecithin + tristearate (Pernetti, Malssen, Van Kalnin & Flöter, 2007), etc., and the stacking of two molecules does not quite predict how large numbers of these molecules assemble (Bot, Veldhuizen, den Adel, & Roijers, 2009). Among these systems, only ethyl cellulose (Gravelle et al., 2012; Laredo et al., 2011; Zetzl et al., 2012), the mixtures of β -sitosterol + γ -oryzanol and lecithin + tristearate were food-grade, and the forming gels in edible oil were transparent (Bot & Agterof, 2006; Bot et al., 2008; Pernetti, Malssen, et al., 2007).

Despite having a similar functionality, the structuring mechanism of these systems is rather diverse. Structurants like γ -oryzanol, β -sitosterol or related phytosterols are chemically similar in containing a ring system or a hydroxyl group. The presence of these chemical structures is essential for the gel-forming capability of the system (Bot & Agterof, 2006). While agents like lecithin, sorbitan tristearate, vegetable waxes (Hwang et al., 2012), polycosanol (Lupi et al., 2012) and fatty acid are chemically similar in containing one or two long alkyl chains. The latter kind of structural agents may structure oil by the well-known crystallization behavior of the saturated fatty acid chains that also plays a role in regular triglyceride crystallization (Bot et al., 2008).

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The present work investigates the structuring potential of the mixture of sitosterol and lecithin in edible oil (sunflower oil). Both of these structurant have a history of consumption: sitosterol occurs naturally in many vegetable oils and lecithin is commonly used as emulsifier and crystal habit modifier (Garti, Schlichter, & Sarig, 1986; Vanhoutte, Fourniat, Duplacie, Huyghebaert, & Dewettinck, 2002). Considering the nutritional value of sitosterol and lecithin (Lau, Journoud, & Jones, 2005; Zhang, Wang, & Beitz, 2006), successful preparation of organogels with them is not only able to structure edible oil as an alternative to crystalline fat but also has desirable health benefits. This characteristic sets this type of structurant apart from the nonedible component-based structuring-oil systems, such as ricinelaic acid (Wright and Marangoni, 2006, 2007) and 12-hydroxystearic acid (Rogers et al., 2008).

Given the molecular structural differences between sitosterol and lecithin, and the fact that detailed information on their oil-structuring capability is lacking, it is of interest to identify the opportunities and limitations of this particular oil structuring system. To do this, a number of sitosterol + lecithin mixtures were screened in this work. A relatively high concentration of structurant (16%, w/w) was used in order to further understand the structure and its formation. Since an understanding of rheology is critical in optimizing final quality of organogel, the rheological properties were investigated in detail for the final organogels developed with S and L at three temperatures for ten days. Previously, it was found that the rheological behavior of plastic fats is governed by interactions between fat crystals in an aggregated three-dimensional, solid-liquid matrix (Herrera & Hartel, 2000). Therefore, the microstructure of crystal network in some selected organogels was also investigated in this study, and connected it with the differences of the rheological behavior.

2. Materials

2.1. Oil phase

All experiments were performed on samples in which the continuous phase was formed by sunflower oil (SO, high in linoleic acid content). The major fatty acid present in SO determined by GC-MS was linoleic acid with 55.95% (sd = 0.03), followed by 27.24% oleic acid (sd = 0.06), 6.12% palmitic acid (sd = 0.12), and 5.01% stearic acid (sd = 0.27).

2.2. Structurant

The structurants we used were sitosterol ([83-46-5], 75% purity, Aladdin Reagent Database Inc.) and lecithin ([8002-43-5], 98% purity, Aladdin Reagent Database Inc.). The structurants were used without further purification. The sitosterol sample had a melting point of 120–143 °C and the lecithin had a melting point of 135–139 °C (given by the supplier). The structurants were combined in various ratios to form organogels. In this work the composition of the structurant will be described as the mass ratio sitosterol:lecithin, or in short S:L.

3. Methods

3.1. Sample preparation

Clear solutions of 16% (wt.%, based on oil) sitosterol and lecithin in sunflower oil were prepared by dissolving the weighed structurant in a weighed amount of oil at a temperature of 90 °C (based on the preliminary experiment result, the mixture system, i.e., sitosterol + lecithin or sitosterol dissolved in sunflower oil, could form a eutectic solution at this temperature, data not shown). The transparent solution was stirred while heating for 40 min. Samples were made with sitosterol:lecithin mass ratios of 0:10, 6:4, 7:3, 8:2 and 10:0 (i.e., S0L10, S6L4,

S7L3, S8L2 and S10L0) at 16% total structurant concentration (as default). All concentrations mentioned here are expressed as weight percentage. Samples of these solutions were stored overnight at 5 °C in a standard fridge (this condition provides an average cooling rate of about 10 °C/min) and then stored in incubator (temperature control range 0–60 °C with an accuracy of ± 0.5 °C) for ten days at three T_s of 5 °C, 15 °C and 25 °C, respectively.

3.2. Rheology

The rheological measurements of sitosterol + lecithin oil organogels, developed at three storage temperatures (5 °C, 15 °C and 25 °C) were performed in a controlled-stress rheometer (RheoStress 600, Haake, Karlsruhe, Germany), equipped with a cone sensor (C35/1° Ti; 35 mm diameter, 1° angle) with 0.052 mm gap. The sample compartment was controlled at a temperature of 25 °C using a water bath/circulator Haake DC-30 and a Haake Universal Temperature Controller System (UTC RS600) (Haake, Karlsruhe, Germany). The composition and temperature dependences of the storage modulus (G') and loss modulus (G'') for organogels were measured by applying a frequency sweep between 0.1 Hz and 10 Hz at a fixed shear strain (0.01%) within the linear viscoelastic region, and the complex modulus (G^*) and the phase angle (δ) values at a constant frequency (1 Hz) for different samples were calculated. The composition dependence of G' organogels developed at different T_s was acquired from frequency sweep at 1 Hz, strain of 0.01%. The strain dependence of G' for organogels was conducted at a fixed frequency (1 Hz) to examine the maximum strain at which the organogel network was ruptured. At a given $T_s = 5$ °C, the temperature dependence of the elastic modulus for organogels was determined at a heating rate of 5 °C/min from 5 °C to 90 °C with a frequency of 1 Hz, strain 0.01%. The effect of heating rate on the elastic modulus for organogels was performed at heating rate of 1 °C/min and 5 °C/min from each given T_s (5 °C, 15 °C or 25 °C) to 90 °C with a frequency of 1 Hz and strain of 0.01%.

3.3. Optical analysis

Polarized light microscopy (PLM) was used to examine the morphology of the crystallized systems. To guarantee a uniform sample thickness, two cover slips were glued to a glass microscope slide with a distance of 2.2 cm between them. The sample (90 °C) was placed within this gap of a preheated (≈ 90 °C) glass slide, and a glass cover slip was placed over the sample such that it rested on the glued cover slips. Samples of these solutions were stored overnight at 5 °C in a standard fridge and then stored for ten days at three T_s (i.e., 5 °C, 15 °C and 25 °C). Photomicrographs as a function of storage temperature (T_s) were obtained of the slide, with a polarized light microscope (Axioskop 40 Pol/40 A Pol, Zeiss) equipped with a color video camera.

3.4. Statistics

An analysis of variance (ANOVA) of the data was performed, and a least significant difference (LSD) was used to compare the means. Data were also graphed using Graphpad with error bars indicating standard error from the mean.

4. Results and discussion

The gel formed or not significantly depends on the mass ratio between S and L after being stored at three T_s (5 °C, 15 °C and 25 °C) for ten days. As the mass ratio of S increased, organogel systems underwent a transition from yellow to milk white, and the transparency gradually reduced. Based on the visual appearance of the systems developed after ten days of storage at three different T_s , when mass ratio of S was below 60% in mixed structurant, there might be some sedimentation of crystals in these supersaturated solutions, but not at a sufficient

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