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Phytosterols-induced viscoelasticity of oleogels prepared by using monoglycerides

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ABSTRACT

Monoglycerides (MGs) and phytosterols (PS) are known to form firm oleogels with liquid oil. However, the oleogels are prone to undergo polymorphic transition over time that lead to crystals' aggregation thus, compromises physical properties. Thus, we combined MGs with PS to control the crystallization and modify the morphology of the combination oleogels, as both components are reported to interact together. The oleogels were prepared at different ratio combinations and characterized in their rheological, thermal, morphology, and diffraction properties. The results showed that the 8:2 MGP:PS exhibited higher storage modulus (G′) than the MGP mono-component. The combination oleogels exhibited effects on the crystallization and polymorphic transition. Consequently, the effects led to change in the morphology of the combination oleogels which was visualized using optical and electron microscope. The resultant effect on the morphology is associated with crystal defect. Due to observable crystals of MGP and PS, it is speculated that the combination oleogels formed a mixed crystal system. This was confirmed with diffraction analysis in which the corresponding peaks from MGP and PS were observed in the combination oleogels. However, the 8:2 oleogel exhibited additional peak at 35.41 Å. Ultimately, the 8:2 was the optimum combination observed in our study. Interestingly, this combination is inspired by nature as sterols (phytosterols) are natural component of lipid membrane whilst MGP has properties similar to phospholipids. Hence, the results of our study not only beneficial for oil structuring, but also for the fields of biophysical and pharmaceutical.

1. Introduction

An oleogel is a self-assembled structure formed by the entanglement of one or more structuring units such as crystals, fibrillar networks, or suspended polymer strands. The use of oleogels provides an alternative to saturated and trans-fat usage in conventional lipid-based food products. Different approaches and techniques have been discovered recently which spans from mono component to mixed component oleogels (Blach et al., 2016; Davidovich-Pinhas, Barbut, & Marangoni, 2016; Gravelle, Davidovich-Pinhas, Zetzl, Barbut, & Marangoni, 2016; Lopez-Martinez, Charo-Alonso, Marangoni, & Toro-Vazquez, 2015; Patel, Babaahmadi, Lesaffer, & Dewettinck, 2015; Patel, Schatteman, De Vos, Lesaffer, & Dewettinck, 2013; Patel, Schatteman, Lesaffer, & Dewettinck, 2013; Patel et al., 2014). Approaches to structure oils with crystalline non-fat particles have gained considerable interest among food scientists as these systems closely resemble conventional fat structured systems (Bot & Agterof, 2006; Doan, Van de Walle, Dewettinck, & Patel, 2015; Lopez-Martinez et al., 2015; Patel et al., 2015). The quest to find new edible structurants has become more challenging due to the regulatory approval of chemical compounds that typically create good oleogels but with restricted edible applications.

Monoglycerides (MGs) are lipid molecules consisting of single fatty acids esterified to the glycerol backbone. Different MGs vary in their type and length of carbon chain of fatty acids. MGs when dispersed in oil, form an elastic gel upon cooling to the Krafft temperature (Chen & Terentjev, 2009; Chen, Van Damme, & Terentjev, 2009; Verstringe, Moens, De Clercq, & Dewettinck, 2015). MGs can create four different phases when dissolved in a hydrophobic matrix (oil):

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isotropic, inverse lamellar, sub-α crystalline, and β-crystalline phases (Chen et al., 2009). Upon cooling, MGs first form an inverse lamellar phase in which the glycerol heads are densely packed in a hexagonal manner in planes in the middle of bilayers. Below the crystallization point, lamellar phases transform into the sub-α crystalline phase with aliphatic chains packed in an orthorhombic configuration. The gel-like properties of those two phases are similar with no significant difference in the rheological response (Chen et al., 2009). However, both phases are only metastable and tend to transform into a triclinic packing of MGs resulting in a β-crystalline phase (Chen & Terentjev, 2009; Ojijo, Kesselman, et al., 2004).

Monoglyceride oleogels in the β-crystalline phase exhibit large crystal aggregation, which compromises the oil binding capacity of the gel (Chen & Terentjev, 2009). Namely, the β-crystalline phase formation causes a separation of the D- and L-isomer of monoglycerides (Chen & Terentjev, 2009). Several studies have therefore focused on controlling the crystallization and polymorphic behavior of monoglycerides in oil to mitigate this undesired aggregation by for example applying shear nanostructuring (Da Pieve, Calligaris, Co, Nicoli, & Marangoni, 2010) or by combining monoglycerides with ethylcellulose (Lopez-Martinez et al., 2015). Ethylcellulose can bind with monoglycerides through hydrogen bonding and as such modify its crystallization behavior. The addition of ethylcellulose also improves the rheological properties of oleogels (Lopez-Martinez et al., 2015).

Phytosterols (PS) are naturally occurring cell wall stabilizing components in plants that are commercially used as cholesterol-lowering agents. β-Sitosterol is the most common PS and exists in 3 different crystalline forms: anhydrate, hemihydrate, and monohydrate, depending on the water content (Christiansen, Rantanen, von Bonsdorff, Karjalainen, & Yliruusi, 2002; von Bonsdorff-Nikander et al., 2005). Similar to cholesterol (COH), PS is a sterol based molecular structure consisting of a steroid skeleton with a hydroxyl group attached at the carbon number 3 (C-3) of the A-ring and aliphatic side chain at carbon number 17 (C-17) of the D-ring (Moreau, Whitaker, & Hicks, 2002). In oil structuring, β-sitosterol and γ-oryzanol have been shown to form unique structures in canola oil that are capable of trapping oil via capillary action between the self-assembled γ-oryzanol and β-sitosterol co-crystals (Bot & Agterof, 2006; Bot, den Adel, & Roijers, 2008; Co & Marangoni, 2012).

The ability of γ-oryzanol and PS to co-crystallize and form hollow tubules with 10.9 nm diameter and 1.5 nm wall thickness, explains why the combination is capable of immobilizing liquid oil (Bot et al., 2012). These tubules may co-assemble and create a continuous three-dimensional network over macroscopic length scale with non-polar solvent immobilized internally (Bot & Flöter, 2011). Bot and Agterof examined a series of sterols and found that dihydrocholesterol, cholesterol, β-sitosterol, and stigmasterol produced firm oleogels. They concluded that the presence of the hydroxyl group was critical for the formation of the gel. The ring structure with no double bonds accelerated the gel formation, whereas a double bond resulted in no gel formation (Bot & Agterof, 2006; Bot, den Adel, Roijers, & Regkos, 2009). PS have also been combined with other compounds. For instance, Han et al. studied the structuring properties of a sitosterol and lecithin mixtures. Their findings suggest that lecithin induced a change in the assembly of β-sitosterol in high linoleic sunflower oil (HLSO) and altered the physical properties of oleogels (Han et al., 2014).

Comprehensive understanding of the effect of cholesterol on the phospholipid membrane acts as a basis to hypothesize that a combination of MGs and PS may produce mixed-component oleogels with higher elastic/storage modulus (Bin Sintang, Rimaux, Van de Walle, Dewettinck, & Patel, 2017; Kouzounis, Lazaridou, & Katsanidis, 2017; Lopez-Martinez et al., 2015; Yang, Chen, & Yang, 2017). Since, cholesterol improves the physical properties of phospholipid membrane, by condensing (chain ordering) alkyl tails of phospholipids (Cao, Tokutake, & Regen, 2003). The formation of mixed-component oleogel is based on the ability of MGs and PS to form hydrogen bonding, forming complexes with different thermal behavior (Gater et al., 2013). In this article, we prepared the oleogels by reducing the ratio of MGs and replaced with PS, whilst the total concentration was remained constant. The present paper reports some novel findings on the effects of oil structuring properties, crystallization process, morphology, and diffraction properties of combination oleogels. In addition, we addressed the possible interaction which provides explanation to the improvement in oil structuring properties of MGs, PS and their combinations reported earlier (Bin Sintang et al., 2017). The combination of PS and MGs offers an interesting food-grade oil structuring alternative to saturated fats and encourage further exploration of potential application of PS.

2. Materials and methods

2.1. Materials

Refined sunflower oil and monoglycerides from hydrogenated palm oil (MGP) ($C_{16:0}$; 59.1%, $C_{18:0}$; 38.5%) were supplied by Vandemoortele Lipids N.V., Belgium. CardioAid™ (non-esterified phytosterols including 50.4% β-sitosterol, 25.0% campesterol, and 15.3% stigmasterol) was provided by ADM (USA).

2.2. Oleogel preparation

Oleogels were prepared by using MGP, PS, and combinations thereof in ratios of 10:0, 8:2, 7:3, 6:4, and 0:10 (wt%) in sunflower oil. The total structurant(s) concentration is 10 wt%. The mixture was first heated to 100 °C under continuous stirring for approximately 20–30 min using a magnetic stirrer (Model EM3300T, Labotech Inc., Germany) followed by cooling at room temperature for 20 min. The samples were finally stored at 5 °C for one-week. An oleogel of MGP mono-component at 6 wt% (6:0) was prepared for thermal study.

2.3. Rheological measurement

The linear viscoelastic region (LVR) of the prepared oleogels were measured by small amplitude dynamic measurement using the rheometer AR 2000ex (TA Instruments, New Castle, DE) with the Advantage application software. The experiment was performed using 40 mm cross-hatched parallel-plate geometry and a gap size of 1000 μm. Frequency sweep tests (1 to 100 Hz) were conducted at constant stress value in the linear response region (oscillatory stress = 4 Pa). The measurement was conducted in triplicate at 5 °C after one week stabilization time.

2.4. Differential scanning calorimetry (DSC)

The crystallization kinetics in the different mixed oleogels were analyzed using Q1000 DSC (TA Instruments, New Castle, DE). The DSC was calibrated with indium (TA Instruments, New Castle, DE), azobenzene (Sigma-Aldrich, Bornem, Belgium) and undecane (Acros organics, Geel, Belgium) before analysis. The oleogels of MGP, PS, and their combinations prepared at a total structurant of 10 wt% were sealed in hermetic pans, and an empty pan was used as a reference. The samples were heated to 150 °C and held for 2 min to eliminate crystal history, followed by a cooling step to 5 °C (at 10 °C/min). The samples were then kept isothermal for 1 h and 5 h before heating to 150 °C (at 5 °C/min). The same pans were kept for one week at 5 °C before heating to 150 °C (at 5 °C/min). For better illustration of the effect, 6 wt% (6:0 MGP:PS) of MGP mono-component was studied using the same procedures. All the analysis was done in triplicate. The comparison between the oleogels was based on peak temperature (crystallization and melting).