



Structural and viscoelastic characterization of ternary mixtures of sunflower oil, saturated monoglycerides and aqueous phases containing different bases



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ABSTRACT

The structure at different length scales and the viscoelastic properties of ternary mixtures composed of saturated monoglycerides, sunflower oil and aqueous solutions of weak bases (KHCO_3 , NaHCO_3 , and NH_4HCO_3) or strong bases (NaOH and KOH) were investigated. The characteristics of ternary mixtures were studied systematically by using polarized light microscopy, differential scanning calorimetry (DSC), synchrotron X-ray diffraction (XRD) and rheological analysis. Results showed that the base type and concentration greatly affected the structure of the mixtures. The use of strong bases allowed gelled systems to be obtained only at low concentrations (<10 mM). On the contrary, the presence of weak bases induced gelling at all concentrations considered (from 1 to 1000 mM). The increase of base concentration led to a reduction of the mean droplet diameter and melting temperature. At the same time, the viscoelastic characteristics as a function of base concentration followed a more complex behavior: G' and G'' progressively decreased as the salt concentration increased in a concentration range from 1 to 100 mM, while the rheological parameters increased when salt concentration increased from 100 to 1000 mM. The structural and viscoelastic behavior of systems prepared with different salts were commonly independent of the cation present in the medium. Results highlight that it is possible to tailor the structure of these gels by using specific bases.

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1. Introduction

The identification of strategies to substitute and/or reduce saturated or hydrogenated fats by using structural design principles is a timely topic. Polysaccharides, proteins, emulsifiers and combinations thereof have been used by different authors to obtain macroscopic structures with similar features to plastic lipid matrices (Batte, Wright, Rush, Idziak, & Marangoni, 2007a and 2007b; Co, & Marangoni, 2012; Chung, Degner, & McClements, 2014; Chung et al., 2013 and 2014; Co, & Marangoni, 2013; Firoozmand, & Rousseau, 2013). The structuring efficiency of these molecules depends on different factors, such as environmental and processing conditions, ingredient ratio, molecular structure and interactions among the structuring agents and other molecules (i.e., electrostatic, hydrophobic, and hydrophilic interactions) (McClements, Decker, Park, & Weiss, 2009).

Among structuring agents, the class of emulsifiers is particularly promising. Owing to their “schizophrenic” character, emulsifiers are able to self-assemble in different distinct environments such as hydrophilic, hydrophobic or a mixture of both. This interesting property is the result of entropy maximization (accompanying the formation of

the smallest possible aggregates) and free energy minimization (for minimal exposure of the hydrocarbon chains). Thus, for a given volume and head-group area, structures satisfying these requirements will form firstly (Hyde et al., 1997). A widely studied class of emulsifier is that of monoglycerides (MG), commercially available with different degrees of unsaturation and chain lengths. Depending on the chemical structure of the MG, the temperature and presence of other ingredients, monoglycerides can form different mesophases when hydrated (Krog, & Sparsø, 2004; Krog, & Larsson, 1968, 1973; Heertje, Roijers, & Hendrickx, 1998). When binary MG-water systems are heated above the Krafft temperature, the hydrocarbon chains convert to a disordered state and water penetrates among the ordered polar groups. Finally, up to three liquid crystalline phases, namely lamellar, inverted bicontinuous and hexagonal phases, can form (Larsson, 2009).

Considering the mesomorphic behavior of saturated monoglycerides, the lamellar phase made of double layers of lipid molecules separated by water layers seems to be particularly promising in food formulations. In particular, the liquid crystalline lamellar phase converts into the so called α -gel phase when temperature is reduced to below the Krafft temperature. The α -gel phase can also transform to the coagel phase, made of a network of plate-like β -crystals (Heertje et al., 1998). The peculiarity of this system is that monoglyceride

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lamellar bilayers can create a shell entrapping a high quantity of a third lipophilic component, such as oils. From a practical point of view, the resulting system is a gel with fat-like aspect and can be used as saturated fat substitute or to reduce the total fat content of a food product (Batte et al., 2007a and 2007b). Promising results have been obtained in the attempt to replace plastic fats, such as palm oil, with MG-gels in bakery products (Goldstein, & Seetharaman, 2011; Manzocco, Calligaris, Da Pieve, Marzona, & Nicoli, 2012; Calligaris, Manzocco, Valoppi, & Nicoli, 2013).

The structure of MG-gels is determined by a wide number of compositional and processing factors, including the composition of the aqueous phase (e.g., pH, salts, proteins), which appears to be one of the principal variables affecting the MG swelling capacity. For instance, the presence of NaCl and/or whey protein greatly affects the lamellar swelling behavior by shielding the electrostatic charge of co-surfactants (Batte et al., 2007b; Mao, Calligaris, Barba, & Miao, 2014). In a recent work, Valoppi, Calligaris, Barba, & Nicoli (2015) studied the complex interplay among MG and milk constituents in the formation of MG-gels. It was observed that both milk proteins and salts greatly affect the swelling capacity of monoglycerides.

The importance of electrostatic interactions in determining the swelling behavior was described by Krog & Larsson (1968). Monoglycerides have a limited swelling capacity due to the long range van der Waals force between lipid bilayers. The introduction of anionic co-surfactants (i.e., free fatty acids) allows surface repulsion on monoglyceride lamellar bilayers to be increased so swelling can be increased (Krog, 1997). In this case, it is evident that the swelling behavior is also dependent on the pH of the aqueous phase: at high pH, the anionic co-surfactants are ionized leading to the repulsion between lamellar bilayers. As pH decreases, the swelling is progressively limited due to the reduction of these repulsive forces. For instance, by using stearic or palmitic acid the pH should be adjusted, generally by using NaOH, to 5–7 to obtain a proper swelling (Heertje et al., 1998). The possibility to exploit MG-gels in food formulations relies on the understanding of the relationship between MG mesomorphic behavior and food components.

The focus of this study was on the effect of anionic salt solutions on MG-gel structure. Anions chosen were derived from weak bases, commonly used in bakery product formulations as leavening agents. To this aim, aqueous solutions containing different concentrations of potassium bicarbonate (KHCO₃), sodium bicarbonate (NaHCO₃), ammonium bicarbonate (NH₄HCO₃) and sodium acetate (CH₃COONa) were considered as water phase in the preparation of MG-sunflower oil–water mixtures. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) aqueous solutions were used as control solutions. The structural and viscoelastic characteristics of ternary mixtures were systematically studied by using polarized light microscopy, differential scanning calorimetry (DSC), synchrotron X-ray diffraction (XRD) and rheological analysis.

2. Materials and methods

2.1. Materials

Myverol™ saturated monoglyceride (MG) (fatty acid composition: 1.4% C_{14:0}, 59.8% C_{16:0}, 38.8% C_{18:0}; melting point 68.05 ± 0.5 °C) was kindly offered by Kerry Ingredients and Flavour (Bristol, United Kingdom). Sunflower oil was purchased in a local market. Sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonium bicarbonate (NH₄HCO₃), sodium acetate (CH₃COONa), palmitic acid, and stearic acid were purchased from Sigma Aldrich (Milano, Italy). Potassium bicarbonate (KHCO₃) was purchased from J.T.Baker (Deventer, The Netherlands). All solutions were prepared using milli-Q water.

2.2. Sample preparation

2.2.1. Monoglyceride ternary mixture

Monoglyceride hydrogels were prepared using a constant ratio among ingredients:

- lipid phase: 36.4% (w/w) sunflower oil
- water phase: 56.4% (w/w) of aqueous solutions containing 1, 10, 100 and 1000 mM of NaOH, KOH, KHCO₃, NaHCO₃, NH₄HCO₃, or CH₃COONa
- monoglyceride-cosurfactant (CO–MG) mixture: 7.2% (w/w) of MG–cosurfactant mixture made of MG mixed with palmitic and stearic acid in a ratio of 10:1:1 (w/w).

The water phase and oil–CO–MG mixtures were heated separately to 70 °C in a water bath. After complete melting of CO–MG, oil and water phases were mixed and then homogenized using a high speed homogenizer DI 25 (Ika-Werke, Staufen, Germany) at 59,000 ×g for 1 min while maintaining the temperature at 70 °C. Subsequently, the mixture was cooled in an ice bath and then stored at 4 °C for 24 h before analysis.

2.2.2. pH

pH was measured using a Basic 20 pH meter (Crison Instruments, S.A., Barcelona, Spain) mounted with an electrode for solids (52–32, Crison Instruments, S.A., Barcelona, Spain). Standard calibration was done using three different buffers at pH 4, 7 and 9. All measurements were made at 25 °C.

2.2.3. Visual appearance

The visual appearance of the samples was recorded 24 h after preparation. The sample was turned upside down and considered as a gel when it did not flow or flowed only slightly and as a liquid emulsion when it easily flowed. Finally, phase separation indicated when the sample was made of two distinct phases.

2.2.4. Viscoelasticity analysis

A Stresstech Rheometer (Reologia Instruments AB, Lund, Sweden) with application software Stresstech v.4 was used to determine the storage (G'), the loss modulus (G'') and the complex dynamic module (G^*). The measurements were performed in a 40 mm parallel-plate geometry system. The temperature control was obtained by means of a circulating coolant connected to a thermostat. Aliquots of about 4–5 g of gelled sample were placed on the temperature-controlled measuring plate and the measuring gap was set at 2 mm. To determine the linear viscoelastic region for the samples, dynamic stress sweep measurements at a frequency of 1 Hz from 0.1 Pa to 100 Pa were conducted at 20 °C. G' , G'' and G^* moduli were obtained for a frequency scan from 0.1 to 10 Hz using a fixed stress value included in the linear viscoelastic region. Finally, G^* modulus as a function of frequency (ω) was used to calculate the number of rheological units (z) and their strength (A) as reported by Gabriele, de Cindio, & D'Antona (2001) (Eq. 1).

$$G^* = A\omega^{1/z} \quad (1)$$

2.2.5. Microscopy

Samples were analyzed using a polarized light (PL) optical microscope (Leica DM 2000, Leica Microsystems, Heerburg, Switzerland) connected with a Leica EC3 digital camera (Leica Microsystems, Heerburg, Switzerland). One drop of the sample was placed in the middle of a glass slide and a glass cover slip was centered above the drop. Samples were analyzed at room temperature using a 200× magnification. Images were acquired and processed using the application software Leica Suite LAS EZ (Leica Microsystems Heerburg, Switzerland). Images were saved in *jpeg* format with a resolution of in 2048 × 1536 pixels.

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