

Rheological properties of β -sitosterol and γ -oryzanol organogels

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ABSTRACT

The aim of this work was to study the rheological properties of sunflower oil organogels, produced with β -sitosterol and γ -oryzanol, in comparison with the rheological properties of butter, in order to identify the most suitable structures to be used in a baked product. OGs were prepared by dispersing different sterol amounts in warm sunflower oil (75°C) reaching final concentrations of 3.1, 3.5, 4.0, 4.5, 5.0, 5.5, 5.9%, while maintaining a 2:3 ratio (w/w) between the two sterols. Gel formation occurred at all the gelator concentrations and the samples had different rheological properties. All gels showed a solid-like structure with storage modulus (G') higher than loss modulus (G'') and a shear thinning behaviour as complex viscosity decreased when frequency increased. G' and G'' were affected by the gelator concentration, with a sharp increase of both moduli from 4.0 to 4.5%. Moreover, OG prepared with 4.5% gelator concentration showed mechanical spectra similar to those of butter.

1 Introduction

For long time, fat structuring has been a big challenge, because the physical state of fats has a deep impact on the properties of food products. In the past ten years, the attempt of substituting saturated traditional fats with structured fatty materials has been thoroughly studied (Pernetti et al., 2007; Hughes et al., 2009). However, applications of these materials in foods have been little evaluated, in particular in baked products (Nakano & Masaki, 1989; Goldstein & Seetharaman, 2011; Manzocco et al., 2012).

Different compounds have been added to a liquid oil in order to structure it by forming an organogel (OG). An OG is an organic liquid entrapped within a thermoreversible, three-dimensional gel network, formed by the self-assembly of gelator molecules. Successful structuring agents form small and preferably non-spherical building blocks so that network connections can be established on a higher specific surface area (Abdallah & Weiss, 2000; Wright & Marangoni, 2007; Bot et al., 2009b). Systems offering high potential in food applications are the OGs based on a combination of different phytosterols as gelators (Hughes et al., 2009). Sunflower oil OGs, in particular, besides their technological aspects, have interesting nutritional benefits: anti-oxidant and anti-cholesterolemic activities due to the gelator features (Bot et al., 2009b), and a polyunsaturated fatty acid rich profile, brought by the sunflower oil.

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2 Materials and Methods

2.1 Organogel preparation

Organogels (OGs) at different sterol concentrations (3.1, 3.5, 4.0, 4.5, 5.0, 5.5, 5.9%) were prepared using β -sitosterol (Novachimica Srl, Cinisello Balsamo, Italy) and γ -oryzanol (Jan Dekker International BV, Wormerveer, Netherlands) in a 2:3 ratio (w/w). Sterols were dispersed in warm sunflower oil (75°C) and stirred until obtaining a clear solution. The material was then poured in small hinged-lid containers (25 g each) and stored at 4°C for 1 week.

2.2 Rheological measurements

The rheological behaviours of OGs and butter (F.lli Galbusera, Casatenovo, Italy), previously conditioned at 25°C for 30 min, were evaluated using a Physica MCR 300 rheometer (Anton Paar, Graz, Austria), supported by Rheoplus/32 software (v. 3.00, Anton Paar Germany GmbH, Ostfildern, Germany) and equipped with a 25 mm serrated parallel plate geometry (PP25), gapped to 1 mm. Frequency sweep tests were carried out at 25°C, with 0.01% strain, over a frequency range of 0.01-10 Hz. These test conditions were chosen within the linear viscoelastic range, previously checked by means of strain sweep tests performed at 25°C, with a frequency of 1 Hz and ranging the strain from 0.001 to 100%. All these evaluations were carried out in triplicate.

3 Results

The different sterol concentrations yielded both highly and weakly structured OGs. The rheological behaviours of OGs and butter are reported in Figs. 1 and 2.

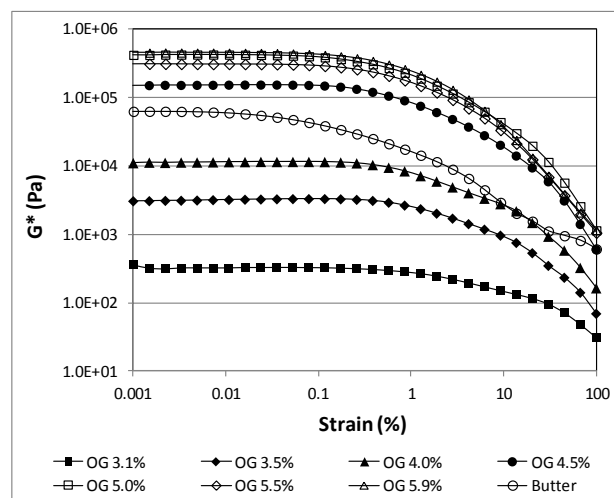


Fig. 1 Strain sweep curves of the organogels (OG) and butter (G^* , complex modulus).

As it can be observed by the complex modulus (G^*) measured as a function of strain (Fig. 1), the most structured materials were obtained with gelator concentrations higher than 4%. These materials maintained their structure until a strain of about 0.1%. On the contrary, the weakly structured OGs, being more viscous, were able to stand a higher degree of deformation: their structure, in fact, broken at a strain of about 0.5-0.8%. In terms of G^* values, butter showed an intermediate rheological behaviour, that was between those of the highly and weakly structured materials. However, at the lowest strains tested, G^* values of butter were very similar to those of the sample prepared with 4.5% gelator. Moreover, butter exhibited the shortest linear viscoelastic region, tolerating a minor value of deformation (about 0.01% strain).

Curves obtained by frequency sweep tests are reported in Fig. 2. All the materials showed a solid-like behaviour, being the storage modulus (G') higher than the loss modulus (G''). In particular, at higher frequencies, all materials exhibited more solid-like characteristics, as also highlighted by the decreasing values of $\tan\delta$, which represents the ratio between G'' and G' . Furthermore, both gels and butter showed a shear thinning behaviour: as frequency increased, complex viscosity decreased.

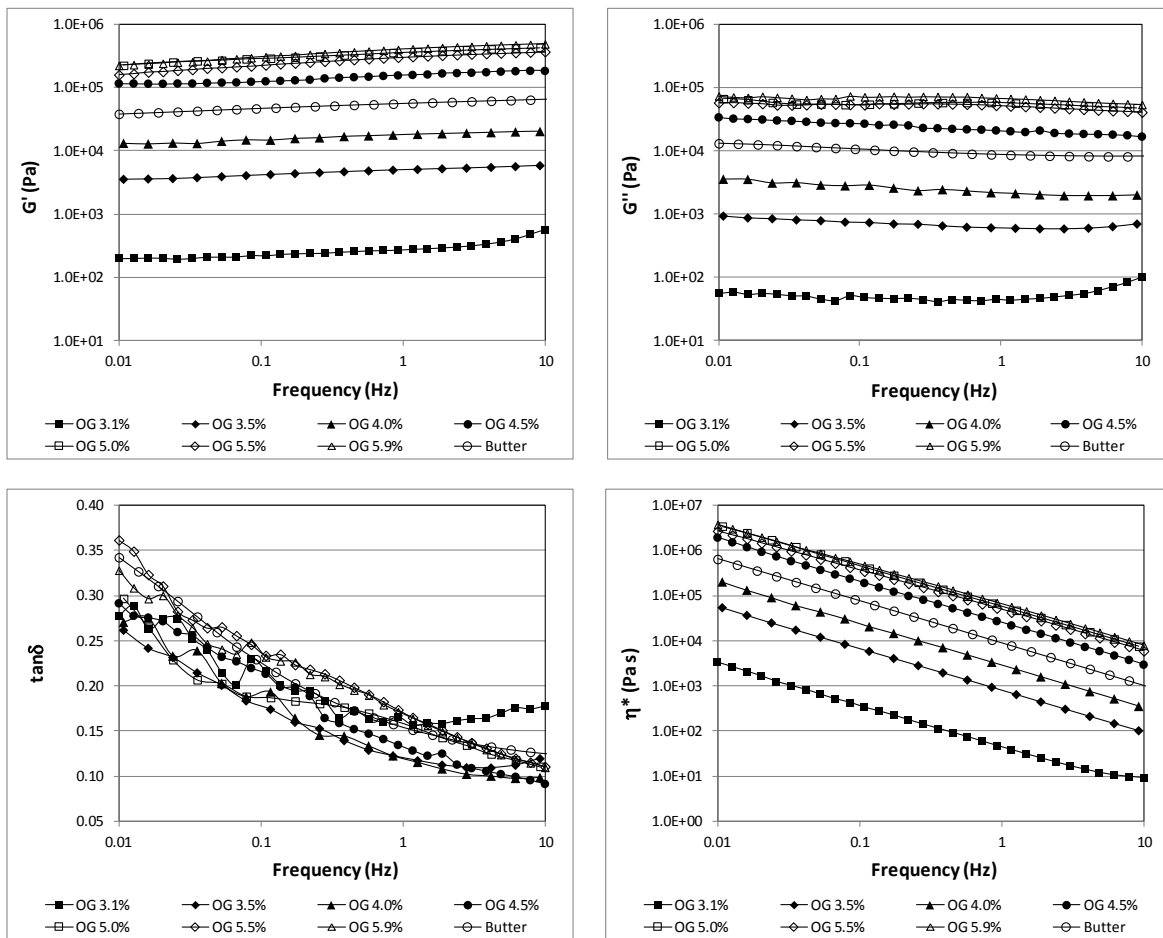


Fig. 2 Frequency sweep curves of the organogels (OG) and butter (G' , storage modulus; G'' , loss modulus; $\tan\delta$, G''/G' ; η^* , complex viscosity).

4 Discussion

The above illustrated rheological characterization confirmed what was already reported in the literature (Bot & Agterof, 2006; Sawalha et al., 2011): consistency of OGs increased with the increase of gelator concentration. In particular, observing the strain sweep curves, it can be noticed that OG 3.1% was by far the least structured material, showing the lowest G^* values. Its viscous nature was also evidenced by the longer linear viscoelasticity region. A broad increase in complex modulus values was observed when the gelator supplementation passed from 4.0 to 4.5%, indicating a better structuring capacity in presence of phytosterol concentrations higher than 4.0%. Actually, several studies indicated gelator percentages ranging from 6 to 25% in order to obtain gels resembling blocks of fat (Bot & Agterof, 2006; Duffy et al., 2009; Sawalha et al., 2011). In our case, gelator concentrations ranging from 5.0 to 5.9% resulted in materials with very similar rheological properties.

The scientific literature also reports that different concentrations of phytosterols do influence the rheological properties of OGs, but not the effective formation of the nano-tubules, the base components of these materials (Bot et al., 2009a). In fact, as already stated, all the OG mechanical spectra highlighted a solid-like behaviour, indicating the formation of a stable structure.

Since the aim of this study was the identification of the OG most suitable for baking, the rheological properties of OGs were compared to those of butter. In fact, in a sweet baked product (such as cakes, biscuits, pastries and croissants), the physical and chemical characteristics of fats used are crucial in determining the quality of the end product. In particular, the physical status of the fat plays a major role in the aeration of the baked product (Podmore, 2002): fat must be solid so that air bubbles do not escape from the batter, but also plastic so that it can fold around each air pocket. The material with the viscoelasticity resembling at best that of

butter was the OG 4.5%, even if it resulted slightly firmer. On the contrary, OG 4.0% was quite similar to butter, but probably too soft to guarantee a good air incorporation during a real baking process.

5 Conclusions

The evaluation of the rheological properties of organogels made with sunflower oil and phytosterols (β -sitosterol and γ -oryzanol) demonstrated that it is possible to obtain structured fats with rheological characteristics similar to those of butter. The use of such materials in a baked goods could improve the antioxidant (due to γ -oryzanol) and anti-cholesterol (due to β -sitosterol and unsaturated oil) potentials of these foods. Further studies are in progress in order to assess whether these novel structured matrices may result in baked products having a quality comparable to a butter-based product.

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