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Effect of organogelator and fat source on rheological properties of olive oil-based organogels

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ABSTRACT

Different samples of olive oil-based organogels were prepared by using cocoa butter, a vegetal fat rich in natural saturated components, and monoglycerides of fatty acids as an organogelator agent. Dynamic temperature ramp tests, carried out at 5 °C/min, allowed the determination of rheological characteristics (complex modulus, G*, and phase angle, δ) and onset of crystallisation (T_{co}) of the investigated materials. Experimental results showed that, at a Myverol amount less than 2% (w/w), T_{co} increases with the amount of saturated components in the fat mixture, whereas, increasing the organogelator fraction, T_{co} is only dependent on organogelator concentration. Moreover, a gelation temperature, T_g, corresponding to the dynamic moduli crossover, was observed for all samples with a Myverol content higher than 1.5% (w/w) and it was found to overlap with T_{co} when a critical concentration (ranging approximately between 2.3% and 3%) of the organogelator was exceeded. Rheological parameters are always affected by both oil phase composition and Myverol fraction; G* increases with either Myverol or cocoa butter amount, while the phase angle decreases, evidencing an increase in structure and consistency. The experimental results can be useful to design novel fat systems having the desired macroscopic properties: in fact crystallisation temperature can be set controlling the organogelator concentration whereas dynamic moduli can be properly changed by modifying the saturated-to-unsaturated fatty acids ratio.

1. Introduction

Organogels are solid-like systems based on gelation of organic solvents by means of either low molecular weight components or oil soluble polymers able to build a three-dimensional network which entraps the liquid solvent (Gronwald, Snip, & Shinkai, 2002). The organogelation process is quite similar to the gelation of aqueous systems (hydrogels) resulting from the action of water soluble molecules (such as polysaccharides or proteins) and involves, usually, weak interactions (such as hydrogen bonding, van der Waals force, etc.) among the single units (Kim, Kim, Lee, & Lee, 2010).

The properties of organogels are particularly interesting in different fields, and among the potential different applications, the rheological modification of vegetable oil-based shortenings and the stabilisation of food emulsions are promising techniques adopted to replace, as texturing agents, saturated and *trans* fats in edible oils or food systems (Duffy et al., 2009; Lupi, Gabriele, de Cindio, Sánchez, & Gallegos, 2011).

In fact, many foods (such as ice creams, cheese, baking and confectionery applications) are characterised by the presence of hard fats, able to give the proper texture (Ghotra, Dyal, & Narine, 2002; Marangoni, 2009; Rogers, Wright, & Marangoni, 2009). They are, usually, achieved by catalytic hydrogenation processes (Singh, Rezac, & Pfromm, 2009) that, involving the production of *trans* fatty acids (TFAs), can have negative implications for the human health (e.g. increase in cholesterol levels or contributions to cardio-vascular diseases) (Blanco Muñoz, 2004; Marangoni et al., 2007). As a consequence of these issues, novel fat systems, less dangerous for consumer's health, are now investigated (Marangoni, 2009; Norton et al., 2009; Pernetti, van Malssen, Flöter, & Bot, 2007) and, among them, organogels seem particularly interesting because organic gelators, promoting the formation of a crystalline network, seem able to give the proper "texture" to foodstuffs and to stabilise many heterogeneous systems even at a very low concentration (~0.5–2% w/w) (Hughes, Marangoni, Wright, Rogers, & Rush, 2009; Marangoni, 2009).

In fact, owing to the high viscosity of the gelled oil phase, even large droplets (up to 200 μm) can be stabilised against phenomena such as creaming, coalescence or Ostwald ripening (Hughes et al., 2009). Moreover the three-dimensional crystalline network yields the desired "consistency" to the final product.

Nevertheless, a critical issue for commercial application of these systems is the availability of food-grade organogelators able to create a network similar to the traditional hard fats (Rogers et al., 2009). Different edible gelators were investigated in the literature, such as: triacylglycerols (TAGs), diacylglycerols (DAGs), monoacylglycerols (MAGs) (Calligaris, Da Pieve, Arrighetti, & Barba, 2010; Da Pieve, Calligaris, Co, Nicoli, & Marangoni, 2010; Ojijo, Neeman, Eger, & Shimoni, 2004), fatty acids and

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Table 1
Average composition of adopted cocoa butter (ICAM, 2008).

Fatty acid	Composition (%w/w)
Stearic acid	32–37
Oleic acid	30–37
Palmitic acid	23–30
Linoleic acid	2–4
Arachidic acid	<1
Palmitoleic acid	<1

fatty alcohols (Schaink, van Malssen, Morgado-Alves, Kalnin, & van der Linden, 2007), sorbitan tri-stearate and/or lecithin (Pernetti, van Malssen, Kalnin, & Flöter, 2007; Shchipunov, 2001), sterol and γ-oryzanol (Bot, den Adel, Roijers, & Regkos, 2009), waxes (Toro-Vazquez, Morales-Rueda, Ajay Mallia, & Weiss, 2010) and others. Among them, monoglycerides are particularly interesting because, in addition to their gelling ability, they are also responsible of positive health effects (Goldstein & Seetharaman, 2011).

Da Pieve et al. (2010) used monoglycerides in order to analyse cod liver oil structuration under the effect of shear. Monoglycerides gels were also used by Goldstein and Seetharaman (2011) for producing O/W emulsions as cookies shortenings replacers finding that structured emulsions improved firmness and shelf-life when compared to the unstructured components. Ojijo et al. (2004) studied an olive oil/monoglyceride system by using dynamic and steady temperature ramp tests at different cooling rates. They found that a minimum volume fraction of monoglyceride of 0.025 was necessary to appreciate a storage modulus increase indicating the onset of gelation. Moreover, an increase in the onset of crystallisation temperature was found with the monoglyceride content increase.

Olive oil based organogels were prepared by Lupi, Gabriele, and de Cindio (2011) using a commercial emulsifier (Myverol 18–04K), mainly composed of monoglycerides, and low amounts of cocoa butter. Steady temperature ramp tests were adopted to analyse the viscosity behaviour of organogels with temperature and evidenced an initial increase of the onset of crystallisation (T_{co}) with the concentration of monoglycerides (up to a critical level), followed by an apparent asymptotic value that could be ascribed to a potential saturation effect (Lupi, Gabriele, & de Cindio, 2011). These systems were found suitable to produce oil in water structured emulsions having rheological properties close to commercial margarines (Lupi, Gabriele, de Cindio et al., 2011).

In the present work olive oil/monoglyceride/cocoa butter gels, having formulations similar to the already tested systems (Lupi, Gabriele, & de Cindio, 2011; Lupi, Gabriele, de Cindio, et al., 2011), were investigated by using Small Amplitude Oscillation Tests (SAOTs) aiming at better understanding the role of organogelator and cocoa butter in crystallisation phenomena and their effects on the macroscopic rheological properties at equilibrium conditions.

2. Materials and methods

2.1. Samples preparation

Samples were prepared by using a commercial virgin olive oil (De Santis, Italy), cocoa butter (Icam S.P.A., Italy), monoglycerides of fatty acids (Myverol 18-04K kindly supplied by Kerry Group, Ireland).

According to data supplied by the manufacturers, virgin olive oil is mainly composed of mono-unsaturated fats (about 75% w/w), the rest being saturated (about 15% w/w) and poly-unsaturated fats (about 10% w/w), while cocoa butter (see Table 1) is mainly composed of saturated (56–68% w/w) and mono-unsaturated (31–38% w/w) fats and a lower amount of poly-unsaturated fats (2–4% w/w).

The oil was preheated up to 70 °C in a water bath thermostated by a plate heater (Jolly 2, Falc Instruments, Italy) and then mixed (RW 20, IKA, Germany) with the proper amounts of Myverol 18-04K

Table 2
Samples identification, composition, gelation temperature (T_g), onset of crystallisation temperature in dynamic (T_{co}) and steady conditions (Steady T_{co}). The grey background evidences samples without significant difference ($p<0.05$) between T_{co} and T_g.

Samples ID	Olive oil (%w/w)	Cocoa butter (%w/w)	Myverol (%w/w)	B/O ratio[a] (-)	T_{co} (°C)[c]	T_g (°C)[c]	Steady T_{co}(°C)[b]
B	–	100	–	–	20.3 ± 0.1	N.G.	–
OB1	88.2	11.8	0	0.134	12.2 ± 0.3	N.G.	–
OB2	95.9	4.1	0	0.043	N.C.	N.G.	–
OB3	96.5	3.5	0	0.036	N.C.	N.G.	–
BM1	–	99	1	–	35.4 ± 0.3	31.9 ± 0.5	28 ± 3
BM2	–	98	2	–	39 ± 1	36.2 ± 0.1	–
OM1	99.9	–	0.1	–	N.C.	N.G.	–
OM2	99.5	–	0.5	–	21 ± 1	N.G.	17.7 ± 2.7
OM3	99	–	1	–	30.4 ± 0.8	N.G.	27 ± 1
OM4	98.5	–	1.5	–	36.5 ± 0.1	32.1 ± 0.4	32 ± 1
OM5	98	–	2	–	39.3 ± 0.2	34.9 ± 0.1	–
OM6	97	–	3	–	41.7 ± 0.5	39.9 ± 0.1	41.6 ± 0.5
OMB1	94	4	2	0.043	37.3 ± 0.2	29.4 ± 0.6	38.2 ± 0.9
OMB2	49	49	2	1.000	40.1 ± 0.7	35 ± 1	–
OMB3	4	94	2	23.50	40.2 ± 0.6	37.2 ± 0.3	37.4 ± 0.5
OMB4	94.3	3.4	2.3	0.036	40 ± 1	36 ± 2	38.2 ± 0.4
OMB5	93.0	4.0	3	0.043	44.8 ± 0.6	43.2 ± 0.2	–
OMB6	94.3	2.3	3.4	0.024	46.5 ± 0.1	43.4 ± 0.2	43.4 ± 0.4
OMB7	92.0	4.6	3.4	0.050	46 ± 2	42.9 ± 0.1	–
OMB8	85.2	11.4	3.4	0.134	45 ± 2	42 ± 1	–
OMB9	73.9	22.7	3.4	0.307	44.7 ± 0.1	42.5 ± 0.3	–
OMB10	84.2	11.2	4.6	0.133	46.7 ± 0.7	46.2 ± 0.2	–
OMB11	86.3	3.7	10	0.043	55 ± 2	52.9 ± 0.1	53.5 ± 0.9
OMB12	76.7	3.3	20	0.043	57.2 ± 0.9	55.6 ± 0.2	–
OMB13	67.1	2.9	30	0.043	59.2 ± 0.1	58.9 ± 0.6	–
OMB14	57.6	2.4	40	0.042	60.5 ± 0.1	60.3 ± 0.4	–

[a] Cocoa butter to olive oil ratio in the oil phase.
[b] Data adapted from Lupi, Gabriele, and de Cindio (2011).
[c] "N.C." and "N.G." indicate the absence of crystallisation or gelation, respectively, in the investigated temperature range.