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Non-TAG structuring of edible oils and emulsions

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ABSTRACT

Mixtures of γ-oryzanol and β-sitosterol have been shown to structure pure edible oil phases. This paper reviews the phytosterol system, and compares it with other alternatives to structure edible oils. Furthermore, additional evidence based on small-angle X-ray scattering will be introduced to support the claim that structuring is based on fibril formation (diameter 7.2 nm). Finally, various aspects of the application of phytosterols structuring in water-in-oil emulsions were investigated.

1. Introduction

The field of organogelling has attracted considerable attention in recent years (see e.g. Abdallah & Weiss, 2000; Brizard, Oda, & Huc, 2005; Terech, 1997; Weiss & Terech, 2006). This class of materials is interesting because it raises not only fundamental questions concerning the requirements for their formation, but also because a wide range of potential applications can be identified (including pharmaceutics, food, cosmetics). It would be extremely attractive if ultimately lipid phase structuring could be as versatile as water phase structuring.

The present paper will focus mainly on the properties of a specific example of an organogelling system, the mixture of γ-oryzanol and β-sitosterol in sunflower oil. Before zooming in on this system, however, γ-oryzanol and β-sitosterol based structuring will be discussed briefly in the context of other oil structuring systems involving structurants that are either food grade or very close to such ingredients. A full review can be found elsewhere (Pernetti, van Malssen, Flöter, & Bot, 2007). Subsequently, attention will focus on the structure of the building blocks in the γ-oryzanol and β-sitosterol organogel, and their functionality in oil-continuous emulsions.

2. Structuring edible oils

The benchmark for any form of oil structuring is the gelling of a liquid triacylglycerol (TAG) phase (or oil) by means of a crystalline TAG phase (or fat). This type of system has been studied in great detail and finds wide application in foods (de Bruijne & Bot, 1999; Bot, Flöter, Lammers, & Pelan, 2007; Narine & Marangoni, 1999). Such systems are based on the limited solubility of TAGs rich in longer chain saturated fatty acids (SAFA) and/or mono-unsaturated *trans*-fatty acids in TAGs rich in shorter chain and (poly- and mono-*cis*-)unsaturated fatty acids (MUFA and PUFA, respectively). The crystalline TAG fraction is capable of forming a network of small crystals in the liquid TAG phase. The size of the crystals and the interactions between them determine the mechanical properties of the network.

The crystalline phase is usually prepared by controlled rapid cooling of a warm liquid oil phase to a temperature well below the melting point of the crystalline phase. The crystals are usually relatively large, as can be inferred from the opacity of the gel. The formation of very large crystals is prevented by deep cooling and high cooling rates. This avoids crystallisation conditions just below the melting point of the crystalline phase, where supercooling can

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be achieved relatively easily because nucleation rates are low and crystal growth rates are large. Networks based on small crystals tend to be firmer.

Shear during crystallisation impacts on the interactions between the crystals. TAG crystallisation is a relatively slow process and the crystalline TAG phase is in dynamic equilibrium with the liquid TAG phase. The weak van der Waals interactions between the crystals during the initial stages of crystallisation are therefore quickly complemented by the much stronger connections that are formed when initially separate crystals are linked by crystalline bridges that are deposited at a later stage of the crystallisation process. These 'sintered' connections (cf. Schaink & van Malssen, 2007) are sometimes referred to as primary bonds, and the weaker van der Waals-mediated connections are secondary bonds. The ratio of primary and secondary bonds can be manipulated by the application of controlled shear during the crystallisation process. Networks based on primary bonds tend to be firmer.

The rapid crystallisation of TAGs by deep and rapid cooling usually does not lead immediately to the formation of the most stable polymorphic form and recrystallisation of TAGs during storage is an important phenomenon, therefore. In deep and rapid cooling, TAG crystals usually attain the α modification, a relatively disordered polymorphic form with considerable librational/rotational freedom for the fatty acid chains. Subsequent recrystallisation transforms the structure in the more stable β′ or β polymorphic form, which have much better defined ordering of the fatty acid chains. Structures based on the α polymorphic form are usually soft, possibly due to the weak interactions between crystals, whereas structures based on the β′ or β polymorphic forms are usually firmer.

The wide range of fatty acids that can be found in nature ensures that structuring by means of fat is actually quite versatile. Careful selection of TAG composition, in combination with adequate processing, makes it possible to design networks with a wide range of firmnesses and melting temperatures (de Bruijne & Bot, 1999; Bot, Flöter, et al., 2007).

The major drawback of the use of fat to structure oil phases in food is the fact that this type of structuring is in practice rather dependent on the use of TAGs rich in saturated fatty acids of even chain length 12–16 (lauric, myristic and palmitic acid) and/or *trans*-fatty acids, which are known to contribute to an elevated blood cholesterol level and are therefore associated with a higher risk on cardiovascular diseases (Pernetti, van Malssen, Flöter, et al., 2007). Alternative structurants of edible oils without this drawback would be welcome therefore.

Alternative structurants of edible oils come in a number of classes of compounds (Pernetti, van Malssen, Flöter, et al., 2007). With exception of the dried space-filling protein-stabilised emulsion by Romoscanu and Mezzenga (2006), most systems contain saturated or mono-unsaturated *trans*-fatty acid groups. This leads to communalities in crystallisation behaviour compared to regular TAGs, as is illustrated by the presence of similar β′ and β polymorphs as those occurring in TAG crystallisation. Thus, it is not surprising that it is possible to structure edible oil with with diacylglycerols (DAG), monoacylglycerols (MAG) and fatty acids in a similar fashion as with TAGs (Ojijo et al., 2004; Ojijo, Neeman, Eger, & Shimoni, 2004; Pernetti, van Malssen, Flöter, et al., 2007; Realdon, Ragazzi, & Ragazzi, 2001; Wright & Marangoni, 2006, 2007). Most examples reported in the literature are based on stearic acid fatty acid groups, but compositions based on alternative fatty acid moieties like palmitic acid should be possible too. The analogy with TAG crystallisation suggests that similar structuring functionality is achievable as long as the same amount of crystalline material is used. This opens possibilities to use structurants comprising of mixtures of fatty acid moieties to imitate the melting profiles of TAG mixtures that are used in applications of thermoreversible TAG structuring in food products (de Bruijne & Bot, 1999; Bot, Flöter, et al., 2007). Indeed, Daniel and Rajasekharan (2003), Gandolfo, Bot, and Flöter (2004) and Rogers (2008) have shown that organogelling properties depend on fatty acid chain length.

It is interesting to note that other details of the molecular structure of the structuring agents appear to be less relevant, provided the level of (in)solubility is essentially retained. Structuring has been achieved with wax esters and sorbitan monostearate (Daniel & Rajasekharan, 2003; Murdan, Gregoriadis, & Florence, 1999), ceramides (Rogers, 2008), and it seems possible that for example certain phospholipids, fatty acid esters of propanediol (cf. Abes & Narine, 2007) or sorbitan dialkylates show the ability to structure TAG oils too. Structuring agents like waxes, fatty alcohols, dicarboxylic acids and derivatised FA containing additional moieties like one or two hydroxyl groups or a methyl group are chemically even more different (Daniel & Rajasekharan, 2003; Elliger, Guadagni, & Dunlap, 1972; Gandolfo et al., 2004; Rogers, Smith, Wright, & Marangoni, 2007; Rogers, Wright, & Marangoni, 2008a, 2008b; Tamura, Suetake, Ohkubo, & Ohbu, 1994; Toro-Vazquez et al., 2007).

In contrast, the morphology of the building blocks that form the network in the oil seems to be of greater importance than the details of the molecular structure of the structuring agents. A successful structuring agent forms small and preferably non-spherical building blocks, in order to have a high specific surface area to participate in network connections (see Fig. 1). Often oil structuring agents contain chiral centres if they form high-surface area structures like helical and twisted ribbons (Brizard et al., 2005). In TAG crystallisation, small crystallites are achieved by rapid crystallisation of the fat leading to the formation of small crystallites, and similar processing tricks or storage conditions (Rogers, 2008) may benefit the functionality of structurants based on crystallising fatty acid chains. The effect can be enhanced by the use of appropriate crystal habit modifiers, which automatically brings us in the realm of mixed structuring agents.

Until now, three mixed systems have been identified as capable of structuring edible oil phases: fatty acids + fatty alcohols (Eini & Tamarkin, 2001; Gandolfo et al., 2004; Schaink, van Malssen, Morgado Alves, Kalnin, & van der Linden, 2007), lecithin + sorbitan tristearate (Pernetti, van Malssen, Kalnin, & Flöter, 2007) and phytosterols + oryzanol (Bot & Agterof, 2006; Ritter, van de Sande, & Müller, 1997). Given the huge number of potential combinations, such systems are obviously harder to find. The systems will be discussed in some detail below.

Mixtures of *fatty acids + fatty alcohols* form homogeneous, opaque gels in edible oils upon quiescent cooling, consisting of a particle network at concentrations above ~2% of the structurants (Eini & Tamarkin, 2001; Gandolfo et al., 2004; Schaink, van Malssen, Morgado Alves, Kalnin, & van der Linden, 2007). Gelling of the oil phase has been demonstrated in mixtures in which the fatty alcohol and the fatty acid have the same chain length (16–22), and in mixtures of stearic acid with fatty alcohols of different chain length (16–22). Analogously to regular TAG crystallisation, however, there is every reason to believe that gels can form for somewhat smaller or longer chain lengths (especially if one is not restricted to fridge temperature), and that other combinations of similar chain lengths of fatty acids and alcohols will lead to gel formation. The gels break at a strain of ~10% (Schaink, van Malssen, Morgado Alves, Kalnin, & van der Linden, 2007).

Microscopic images indicate that the alcohol + acid mixture forms much smaller crystals than the pure compounds, especially at ratios around 30% stearic acid + 70% stearyl alcohol (Gandolfo et al., 2004; Schaink, van Malssen, Morgado Alves, Kalnin, & van der Linden, 2007). This is explained by a reduction in the interfacial energy of the nuclei leading to an increase in the nucleation rate, which results in a firmer network based on a larger number of smaller crystals, as is indeed observed. The effect has been