



# Structuring effects of lecithins on model fat systems: A comparison between native and hydrolyzed forms



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## ABSTRACT

Lecithin find a wide spread application in the food industry. The purpose of the work reported here was to systematically map the effects of some commercially available lecithins from different sources (soybean, sunflower, rapeseed), in their native state or hydrolysed form, on the crystallization behavior of model fat systems. To this end, systems based on palm oil as hard fat were studied. Next to macroscopic properties such as product hardness, the crystallization behaviour and the microstructure were studied as a function of time and temperature. Addition of the studied lecithin preparations had a significant influence on the hardness ( $p < 0.05$ ) indicating a structuring effect; this was confirmed by polarised light microscopy and powder X-ray diffraction. The impact of the hydrolysed lecithin was however different from the native one. It was shown that the lecithin hydrophobicity is determinant for the structuring ability.

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## 1. Introduction

The texture of food products based on water in oil emulsions, such as margarine, butter, low fat spreads, shortenings,... is generally provided by the structuring of either the water or the oil phase or both (de Bruijne & Bot, 1999). The oil phase is most of the time structured using triacylglycerols (TAG) hard-stocks that crystallize upon cooling and in this way form a fat crystal network. The macroscopic properties and functionalities of fat-based products are closely related to their microscopic properties: organoleptic properties of the final product, such as the consistency for example, are mostly determined by the structure of the fat crystal network (Danthine, 2012). This structure depends in turn on the size and the morphology of the crystals and on the interactions between them (Van der Waals forces, solid bridges ...) (Johansson, 1995). Crystallization behavior of fats is thus very important to control the quality of fatty products. Emulsifiers are functional additives widely used in the food industry that play a key role during emulsification processes but also improve the texture, stability, volume, softness, aeration and shelf-life of food products (Madsen, 1987). The effects

of emulsifiers on fat crystallization are really variable and depend on several factors (Smith, Bhaggan, Talbot, & van Malssen, 2011). They may act on fat crystallization by promoting or inhibiting fat nucleation, crystal growth, polymorphic transitions and crystal interactions (Garti & Yano, 2001; Perneti, van Malssen, Flöter, & Bot, 2007). The effect of each emulsifier depends notably on the characteristics of its hydrophilic moiety, but also on the length and the structure of the hydrophobic chains. The similarity between the hydrophobic part of the emulsifier and the TAG of the fat blend seems to be a key-element (Cerdeira et al., 2005). In the same way, the miscibility of the emulsifier in the fat blend seems to be determining. Moreover some kinds of emulsifiers crystallize together with the TAG and act as “crystal structure modifiers”, promoting or retarding the polymorphic transformations (Garti & Yano, 2001; Guth, Aronhime, & Garti, 1989). Another effect of emulsifiers can be acceleration of the nucleation rate when they act as seeds for crystallization by crystallizing before the TAG (Katsugari, 1999). On the contrary, they sometimes retard nucleation by perturbing the primary organization of fat molecules (Cerdeira et al., 2005). Another important effect is linked to the adsorption of emulsifiers on the surfaces of the existing crystals, which may retard the crystal growth or modify the growth direction, changing in this way the crystal morphology. It can also change the interactions between the crystals and modify the crystal

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network (Garti & Yano, 2001).

In this context, phospholipids (PL) represent an important class of amphiphilic components, which are highly suspected to influence the crystallization properties of fat systems (Patel & Dewettinck, 2015). According to Smith et al. (2011), phospholipids vary greatly in their interaction with fats. It was both reported that they promote crystallization and that they retard it (Sato & Koyano, 2001; Smith, 2000). Fedotova and Lencki (2010) showed that PL from the milk fat globule membrane or from soy had a significant influence on butterfat crystal morphology, and that the effect was dependent on the PL concentration. They also observed a hardening impact of lecithin, upon addition of 2% of soy lecithin to butter.

There is today an increasing trend to reduce SAFA in foods. Structuring alternatives are desirable. In view of those reports, phospholipids could be used as structuring agents but the real impact of commercially available phospholipids on bulk fat has still to be studied. The terms phospholipids and lecithin are often used interchangeably. Lecithins refer nevertheless to complex mixtures of naturally occurring phospholipids, traditionally obtained by water washing of crude vegetable oils, separation and drying of the gums. Lecithin is thus commonly used to describe a group of commercially available complex phospholipid mixtures.

Therefore, the goal of the work reported here was to systematically map the effect of different commercially available lecithins (=blends of phospholipids) from three vegetable sources (soybean, sunflower, rapeseed). The hardness of bulk model fat systems with and without lecithin addition were measured and compared. Next to this macroscopic property the microstructure development was also monitored to explain the origin of the observed effects. Moreover, apart from the native lecithins, a hydrolyzed form was also considered. Indeed up to now, the impact of a hydrolyzed lecithin on fat crystallization has never been studied and compared to native one.

## 2. Materials and methods

### 2.1. Materials

RBD palm oil was supplied by Lodens Croklaan B.V. (Wormerveer, The Netherlands). Rapeseed oil (RO) was purchased from Vandemoortele (Izegem, Belgium).

The commercial lecithins Semilec (rapeseed lecithin), Verolec (soybean lecithin), Giralec (sunflower lecithin) and Verolec HE60 (Hydrolyzed soybean lecithin) were purchased from Lasenor (Barcelona, Spain).

### 2.2. Blends preparation and samples crystallization

#### Part 1: Quiescent conditions

Two model fat systems, both based on palm oil as hard fat were considered. The compositions of the blends (100% fat) were: Model system 1: 70% palm oil – 30% rapeseed oil; Model system 2: 40% palm oil – 60% rapeseed oil.

The commercial lecithins were added to the above model systems at different levels ranging from 1 to 3% w/w. The properties of the resulting blends were compared to reference products (i.e. without lecithin).

After complete melting of each ingredient, blends were prepared by stirring them for 15 min at 70 °C under constant agitation. Afterward they were poured into small plastic vessels (50 g by vessel). The crystallization was induced by storing the blends at –20 °C for 30 min according to the procedure already presented by Danthine and Deroanne (2003a). After this period, the pre-crystallized samples were transferred to a controlled temperature

cabinet. Model system 1 was stored at 15 °C ± 0.5 °C or 5 °C ± 0.5 °C while Model system 2 was only stored at 5 °C ± 0.5 °C (too liquid at 15 °C). At least two vessels were poured from the same batch and at least two batches were prepared for each set of conditions. All the results presented for each combination of conditions (blend composition, lecithin content, storage duration, storage temperature) are thus averages calculated on, at least, 4 vessels from, at least, 2 batches.

#### Part 2: “Dynamic approach”

In this specific set of experiments, lecithin (Native Soy or HE60 Soy) was added to the same type of fat Models but in different ways (before or after completion of the main crystallization step). All the fats were first heated to 70 °C to ensure complete melting and erase thermal history. The blends were prepared as summarized in Table 1. All the samples (except Condition 1) were stirred using a specific home made device consisting in a cylindrical vessel full of holes in the bottom and an adjusted plunger. During this extrusion-like mixing (always with the same force), fat was forced to pass through those small holes ensuring homogeneous sample even after dilution with liquid oil. All the final compositions were similar to Model 2: 40% palm oil – 60% rapeseed oil. They were all analyzed at 5 °C after 1 week.

### 2.3. Analyses on crystallized samples

After a well define storage period (1 h, 3 h, 24 h, 48 h, 1 week for “Quiescent conditions”; after 1 week for the “Dynamic approach”), the hardness, Solid Fat Content (SFC) by p-NMR (pulse-Nuclear Magnetic Resonance) and, for some conditions, crystal morphology using Polarized Light Microscopy (PLM) and polymorphic state by powder X-Ray Diffraction (XRD) were evaluated.

#### 2.3.1. Hardness evaluation

The hardness (macroscopic property) was measured in a controlled temperature cabinet (15 ± 0.5 °C or 5 ± 0.5 °C, depending on the storage temperature of the samples), using a constant speed penetration test, performed with a SMS texture analyzer TA-XT2i (Stable Micro Systems Ltd, Surrey, UK), as previously described (Brapson-Danthine & Deroanne, 2004). At least three penetration tests were run on each sample (vessel).

#### 2.3.2. Solid fat content (SFC)

The SFC was measured using a pulsed NMR spectrometer (Minispec-mq 20, Bruker, Germany). Automatic calibration was made daily using 3 standards (supplied by Bruker) containing respectively 0.0, 31.3 and 74.8% of solids. The NMR tubes were carefully filled in the controlled temperature chamber using special glass devices designed for sampling crystallized hard fats as previously described (Brapson-Danthine, Gibon, & Deroanne, 2005). Both sampling devices and NMR tubes were put at 15 °C or 5 °C (= storage temperature) before sampling and measuring at the same temperature.

#### 2.3.3. Crystal morphology (PLM)

The crystal morphology of some samples was investigated with a PLM (Nikon eclipse E400) equipped with Basler video camera; the gain was switched in the auto position and images were digitized using the Lucia-G software (LIM, Prague, Czech Republic). The microscope was equipped with a Peltier stage system (Linkam, Scientific instrument Ltd, Surrey, UK), connected to a water-circulating pump (Linkam PE60 temperature controller, Scientific instrument Ltd, Surrey, UK). The samples were evaluated isothermally at their storage temperature (5 °C or 15 °C) (Brapson-

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