



## Structuration of lipid bases with fully hydrogenated crambe oil and sorbitan monostearate for obtaining zero-trans/low sat fats



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### ABSTRACT

Several studies have shown that excessive intake of trans and saturated fatty acids is associated with an increased risk of cardiovascular disease. In this context, the food industry has sought alternatives for the development of healthy lipid bases, with higher levels of unsaturated fatty acids, adapting to current legislation. The incorporation of structuring agents into liquid oils has proven to be a potential alternative for obtaining semi-plastic lipid bases with reduced levels of saturated fatty acids. Thus, the objective of this study was to produce zero trans fat bases with lower saturated fatty acids levels. Palm oil (PO) was used as a zero trans-lipid base reference because of its technological functionality. Blends containing different proportions of high oleic sunflower oil (HOSO) and PO were prepared as follows: control 100: 0; 80:20; 60:40; 40:60; 20:80; and 100: 0 PO: HOSO (w/w%), respectively. Then, 3% of fully hydrogenated crambe oil (FHCO) and 3% sorbitan monostearate (SMS) were added to the blends as structuring agents, forming the structured (S) blends. The addition of HOSO to the PO decreased the saturated fatty acids by up to 30.6%, with consequent increase of unsaturated fatty acids, especially oleic acid. The joint action of the SMS and the FCHO allowed for obtaining structured blends with plastic and spreadability characteristics, as well as modifications throughout the crystallization process of the original blends.

### 1. Introduction

Lipids play important role in human diet, including the supply of energy and nutritional compounds to the organism, besides conferring unique characteristics of texture and flavor to the foods (Gioielli, 1996; Lima, Barros, & Padovesi, 2001). The composition of oils and fats is directly associated with health effects, once studies have shown that the intake of trans and saturated fatty acids may lead to increased risks of cardiovascular diseases and other metabolic disorders (Siraj et al., 2015). Therefore, several authors have sought alternatives for the substitution of saturated and trans fatty acids by lipid bases rich in unsaturated fatty acids, with a potential reduction of health risks (Hunter, 2005; Novello, Franceschini, & Quintiliano, 2010; Watkins, Li, Hennig, & Toborek, 2005). The Mediterranean regions have a low prevalence of cardiovascular diseases due to the high consumption of monounsaturated fatty acids as the main lipid contributor to the diet, especially oleic acid, which has antithrombotic and hypocholesterolemic properties. In addition, oils rich in oleic acid play a key role in

oxidative stability, extending product shelf life (Estruch et al., 2013; Smith, King, & Min, 2007; Willett et al., 1995).

The modification of oils and fats aims to obtain lipid bases with specific characteristics, or tailor made products, for food applications. Zero trans fractions, with lower saturated fatty acids and higher mono and polyunsaturated fatty acids levels, are current examples of this new formulation model (Marangoni, 2012; Rogers, 2009). The possibility of incorporating specific vegetable oils into conventional technical fat formulations stands out as a way to improve the nutritional aspects of lipid-based foods (Gillingham, Harris-Janz, & Jones, 2011).

Palm oil (PO) is widely used in various food products. This raw material stands out for its functional and technological characteristics, high oxidative stability and good availability, therefore it can be an effective alternative for the replacement of partially hydrogenated fats, due to the absence of trans fatty acids. However, its consumption is questioned due to the saturated fatty acids levels in the range of 50%, with possible health risks. In addition, its slow crystallization due to its diacylglycerols composition (4 to 8%) can cause problems in the post-

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processing stages (Mamat, Aini, Said, & Jamaludin, 2005; Marangoni & Narine, 2002; O'Brien, 2009).

Genetically modified sunflower oil is intended to increase the content of monounsaturated fatty acids. High oleic sunflower oil (HOSO) has 75–85% oleic acid and may be an interesting alternative for incorporation into lipid bases due to its differentiated composition and oxidative stability as compared to other vegetable oils. However, most edible vegetable oils, such as HOSO, present a large amount of unsaturated fatty acids, which impairs the crystallization at processing and storage temperatures, thus requiring the use of structuring agents (Cardenia et al., 2011; O'Brien, 2009).

In a technological and commercial approach, oils and fats should exhibit structural and sensory characteristics appropriate to food application and consumer acceptability. Historically, it was understood that crystalline modification in oils and fats would be primarily linked to physico-chemical changes provided by processes such as hydrogenation, interesterification, fractionation and blending, as well as the use of specific time-temperature protocols. However, the reduction of saturated fat in lipid bases for industrial use is not feasible through the use of conventional lipid modification processes, since the potential for reduction of saturated fatty acid levels by these means is significantly limited (Rogers, 2009).

On the other hand, the use of structuring agents, such as specific triacylglycerols, partial glycerides and some emulsifiers, have been indicated as the only viable alternative for obtaining low sat fats with properties compatible with food applications. In recent years, interest in the influence of structuring agents on the physical properties of fatty systems has increased significantly. The modification of physical properties of lipid matrices by means of the structuring approach has proved to be a strategic subject for the processing of high fat foods, aiming at suitability to specific products, reduction of costs, improvement of quality and increase of the applicability and stability of different oils and fats (Wang, Gravelle, Blake, & Marangoni, 2016; Chaves, Barrera-Arellano, & Ribeiro, 2017).

The addition of structuring agents into lipid matrices composed of liquid oils, allows for the production of structured lipid systems, named as organogels, which are characterized by the presence of a small quantity of solid material capable to immobilize a large amount of liquid oil, with functional and technological characteristics similar to plastic fats. As a result, formulations with specific thermal and consistency properties are obtained for product-targeted applications (Marangoni, 2012; Rogers, 2009).

For use in foods, the structuring agents should be food grade, low cost and safe for consumption (Pernetti, van Malssen, Flöter, & Bot, 2007; Rogers, 2009). Several structuring agents are used for the formation of organogels, including monoacylglycerols (Ojijo, Neeman, Eger, & Shimoni, 2004), lecithin and tristearates (Pernetti et al., 2007), waxes (Martini, Carelli, & Lee, 2008), fully hydrogenated oils (Oliveira, Ribeiro, dos Santos, Cardoso, & Kieckbusch, 2015) and others. Structuring elements are usually classified according to their role in the arrangement of the crystal lattice. The first class of structuring elements consists of solid particles dispersed in the oil phase, which forms crystals and initiates the nucleation process and growth of the crystal lattice. The second class refers to the molecular self-assembly, organized in the oil phase to form structures to support the crystal lattice (Dassanayake, Kodali, & Ueno, 2011; Siraj et al., 2015).

The applications of structured fats in foods have been studied for some years, and include the potential use of structuring agents for products such as margarines, bakery products such as biscuits, cookies and cakes, puff pastry and pastes, mayonnaise, sauces, biscuit fillings, toppings, emulsified meat products, processed cheeses, whipped cream, ice creams, chocolate and peanut pastes, among others. In terms of costs, structuring oils and fats appears to be quite similar to the overall costs of conventional mixing and crystallization processes, since it does not require additional technological steps and/or modification of industrial equipment. In general, technological processes are even

facilitated depending on the food product; and the conventional crystallization step can be suppressed in some cases. In this way, the costs of structured fats are mainly related to the choice of oils and/or fats that will be used, as well as the structuring agents used and their respective concentrations. It is important to highlight that the emulsifiers, fully hydrogenated vegetable oils and waxes are commercial products that can be used for structuring lipid matrices at a cost compatible with current industrial fats (Siraj et al., 2015; Wang et al., 2016; Chaves et al., 2017).

In this context, fully hydrogenated vegetable oils, technically referred to as hardfats, have shown to be potentially effective in modifying the crystalline properties of lipid bases, acting as structuring elements to accelerate the crystallization process in systems composed of low and medium melting point triacylglycerols. Hardfats are characterized by a homogeneous fatty acid composition and high melting point triacylglycerols, from the total catalytic hydrogenation of natural oils, being considered low-cost products from the industrial point of view (Oliveira, Ribeiro, & Kieckbusch, 2015; Ribeiro, Basso, & Kieckbusch, 2013).

Fully hydrogenated crambe oil (*Crambe abyssinica* Hochst) (FHCO) contains the behenic acid as the major component, corresponding to 57% of the total fatty acids, as a result of the hydrogenation of erucic acid found in crambe oil, which is unsuitable for human consumption. This fact makes FHCO a product without nutritional restrictions (Guedes et al., 2014; Oliveira, Ribeiro, & Kieckbusch, 2015). Studies have shown the behenic acid as a potential component for the development of low-calorie fats due to its low bioavailability and poor absorption (Kojima et al., 2010; Moreira, Santos, Gambero, & Macedo, 2017).

Sorbitan esters are emulsifiers commonly used in foods. Recent studies have shown this group of compounds as potential structuring agents of vegetable oils, modulating the fat crystallization process. In particular, sorbitan monostearate (SMS) has an odorless, tasteless characteristic and ability to form semi-solid and thermo-reversible organogels. The organization of SMS in the oil phase occurs via the self-assembly mechanism, forming a tubular molecular structure that contributes to the formation of the three-dimensional network, immobilizing the organic fluid represented by the vegetable oil (Rogers, 2009; Smith, Bhaggan, Talbot, & van Malssen, 2011). Recent studies on the structuring effects of SMS suggest its use as a potential structuring element of vegetable oils, through a positive interaction with triacylglycerols (Oliveira, Stahl, Ribeiro, et al., 2015; Cerqueira et al., 2017; Sonwai, Podchong, & Rousseau, 2017). Therefore, the present study aimed to evaluate the structuration of blends containing different proportions of PO and HOSO, using SMS and FHCO as structuring agents, with respect to the physicochemical properties and crystallization behavior of the lipid systems. In addition, lipid bases with lower saturated fatty acids and higher oleic acid, with technological functionality for application in foods will be studied.

## 2. Material and methods

### 2.1. Material

Deodorized palm oil (PO) was supplied by Agropalma S/A, Belém, Brazil; both high oleic sunflower oil (HOSO) and fully hydrogenated crambe oil (FHCO) were supplied by Cargill Agrícola S.A., and sorbitan monostearate was purchased from Sigma Aldrich (SMS, 50% purity; Sigma Aldrich, UK). The raw materials were maintained in a dry place and protected from light until use.

### 2.2. Preparation of the blends

The binary blends PO:HOSO were prepared at the proportions of 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100 (w/w), corresponding to the control samples. The structuring agents were incorporated into the

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