

Señores

Superintendencia de Industria y Comercio

División de Nuevas Creaciones

E. S. D.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 10-092087-00003-0000

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Ref: Expediente No. 10-092.087

Solicitud de registro de patente de invención denominada "PRODUCTO GRASO SÓLIDO CON BAJO CONTENIDO DE GRASA SATURADA Y LIBRE DE ÁCIDOS GRASOS TRANS". Publicada en la Gaceta de Propiedad Industrial No. 622 de 19 de noviembre de 2010, N.P 883.

Solicitante: TEAM FOODS COLOMBIA S.A

SANTIAGO MÁRQUEZ ROBLEDO, identificado con la cédula de ciudadanía número 79.980.922 de Bogotá, portador de la Tarjeta Profesional de Abogado número 131.853 y obrando en mi condición de apoderado de la sociedad SIGRA S.A., atentamente procedo a presentar éste memorial informativo en contra de la solicitud de registro de la patente de invención denominada "PRODUCTO GRASO SÓLIDO CON BAJO CONTENIDO DE GRASA SATURADA Y LIBRE DE ÁCIDOS GRASOS TRANS", solicitada por TEAM FOODS COLOMBIA S.A.

2. Fundamentos de Hecho.

- 2.1. El 28 de julio de 2010 se presentó, ante la División de Nuevas Creaciones de la Superintendencia de Industria y Comercio (en adelante SIC), la solicitud de Patente de Invención titulada: "**PRODUCTO GRASO SÓLIDO CON BAJO CONTENIDO DE GRASA SATURADA Y LIBRE DE ÁCIDOS GRASOS TRANS**", a nombre de la sociedad TEAM FOODS COLOMBIA S.A , organizada y existente de conformidad con las leyes de Colombia.
- 2.2. El objeto de dicha solicitud de patente, de acuerdo con las reivindicaciones de la misma, es "Un producto graso caracterizado porque comprende tres elementos: (1) aceite de palma, (2) aceite líquido y (3) una base grasa constituida por una fracción enriquecida con tripalmitina y/o tripalmitina pura y/o aceite de palma completamente hidrogenado."
- 2.3. Ahora bien, respetuosamente me permito manifestar a ese Despacho que la invención reclamada en la solicitud No. CO 10-092.087 objeto del presente memorial, no cumple con los requisitos exigidos en el Artículo 14 de la Decisión 486, del Acuerdo de Cartagena, que se encuentra plenamente vigente, en el cual se establece lo siguiente:

ARTÍCULO 14 DE LA DECISIÓN 486: *"Los países miembros otorgarán patentes para las invenciones sean de productos o de procedimientos en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial".*

En efecto, de acuerdo con el citado artículo 14, es claro que los países miembros de la Comunidad Andina de Naciones (CAN), que se rigen por la Decisión 486, podrán otorgar el privilegio de patente dentro de su territorio a una invención, siempre y cuando dicha invención tenga novedad, nivel inventivo y aplicación industrial.

- 2.4 En el presente caso, la invención en cuestión No. **CO 10-92087**, carece de la novedad y la altura inventiva requeridas para poder gozar del privilegio de patente solicitado en el territorio Colombiano, como quedará demostrado con los argumentos que se presentan a continuación.

Es bien conocido que la industria de Grasas y Aceites emplea numerosas fuentes de aceites cada una de las cuales en su composición presenta ácidos grasos saturados, monoinsaturados y poliinsaturados. Las principales fuentes con que se cuenta al día de hoy en aceites vegetales son: Aceite de Palma, Aceite de soja, Aceite de Canola, Aceite de Girasol, Aceite de Oliva, Aceite de maíz entre otros.

Cada aceite presenta su propia composición de ácidos grasos los cuales se denominan de acuerdo al número de átomos de carbono.

La mayoría de ácidos grasos presentes en estos aceites, tienen de 4 a 22 átomos de carbono de los cuales los más predominantes son el ácido Láurico (C12:0), Mirístico (C14:0), Palmítico (C16:0), Estearico (C18:0), Oleico (C18:1), Linoleico (C18:2) y linolénico (C18:3) entre otros. El contenido de estos ácidos grasos y la relación entre la cantidad de ácidos grasos saturados e insaturados presentes en una grasa tienen una gran influencia sobre si dicha grasa es sólida o líquida.

A partir de lo anterior, y valiéndose de los diferentes procesos conocidos para el tratamiento de los aceites con los que se cuenta en la industria de las grasas, tales como la hidrogenación, inter-esterificación, fraccionamiento y desodorización la industria de grasas y aceites elabora diversos tipos de productos para hacer frente a las tendencias que se van presentando día a día. Incluso es conocido en el estado del arte que desde hace años ha venido elaborando grasas sólidas con bajos contenidos de grasas saturadas y libres de grasas trans, tal y como se aprecia en los documentos EP 1159877 (D1), WO 96/39855 (D2), US 2006/0051488 (D3), que entre otros documentos anteriores a la fecha de presentación de la solicitud en cuestión en fase internacional (10-01-2008), demuestran la previa existencia de composiciones que incluyen dos o más aceites y/o grasas diferentes para obtener composiciones idénticas a las ahora reclamadas. Así como el documento "Towards a multidisciplinary approach to structuring in reduced saturated fat-based systems – a review". Danisco 2010 (D4), el cual es una revisión en la que se incluyen estudios e información anteriores al 10-01-2008, y que muestra la existencia de las composiciones reclamadas desde antes de la presentación de la solicitud en cuestión.

En efecto, es ampliamente conocido en la industria que en la elaboración de un producto graso con baja cantidad de grasas saturadas se contemplan varias alternativas de mezclar dos o más aceites en diferentes proporciones; uno de los cuales tiene la cantidad más alta de saturados y otro en medio o alto contenido de insaturados dependiendo del contenido final que se quiera obtener en grasas saturadas.

Una de las ventajas de obtener una mezcla de aceites con otro balance de saturados/insaturados es la de someterla a proceso de inter-esterificación que permite obtener modificación en la textura del producto graso para que pueda ser aplicado en la elaboración de varios alimentos.

En la actualidad la Industria de aceites y grasas cuenta con proveedores que mundialmente tienen centros de investigación y que brindan el soporte técnico y la información sobre las tendencias que se van presentando y que son de interés público. Por ejemplo, en el Informe Técnico editado por la empresa Danisco en el 2010, y denominado “Towards a multidisciplinary approach to structuring in reduced saturated fat-based systems – a review”; es un recuento de lo conocido hasta ese momento en la industria de grasas y aceites y en dicho documento se evidencia que ha sido de gran interés para la industria de las grasas y los aceites poder proporcionar composiciones con bajos contenidos de grasas saturadas y libres de grasas trans, adicionalmente, en este documento también se indican las técnicas más ampliamente utilizadas a nivel mundial para la obtención de productos con las características deseadas, dentro de las que se encuentran el mezclado de productos con diferentes contenidos de grasas saturadas y/o insaturadas, para la reducción de los niveles de grasas perjudiciales para la salud, que es exactamente lo que el solicitante de la materia objeto del expediente No. CO 10-092-087, plantea mediante la mezcla de 3 fuentes diferentes de grasas, tal y como se ha venido realizando desde hace varios años y como se demuestra en los documentos del estado del arte y en la revisión hecha sobre el tema por parte de la empresa DANISCO. Por lo tanto, es claro que existen suficientes evidencias dentro del estado de la técnica que demuestran que las composiciones solidas de grasas con baja cantidad de grasa saturada y libres de grasas trans, tales como los productos ahora reclamados en la solicitud de patente en cuestión, los cuales también son mezcla de diferentes tipos de aceites y grasas, ya estaban disponibles desde antes de la presentación de la solicitud Colombiana No. 10-092.087.

3. CONCLUSIONES

Como se ha demostrado, la materia objeto de la solicitud Colombiana No. CO 10-092.087, carece de la novedad y nivel inventivo necesarios para gozar del privilegio de patente solicitado, toda vez que la combinación de aceites y/o grasas que se propone es una combinación que ya había sido previamente revelada y que estaba dentro de lo conocido en el estado del arte, por lo cual una persona medianamente versada en la materia fácilmente podría llegar a obtener las mismas composiciones bajas en grasas saturadas y libres de grasas trans que son ahora reclamadas, a partir de sus conocimientos básicos en la industria de las grasas y de los conocimientos aportados por los documentos que hacen parte del estado de la técnica, dentro de los cuales se han mencionado solo unos pocos.

Respetuosamente le solicito al Despacho tener en cuenta todos los argumentos anteriormente expuesto, así como los documentos técnicos que los respaldan, con el fin de NEGAR la patente de invención solicitada por TEAM FOODS COLOMBIA S.A, teniendo en cuenta que la misma carece por completo de los requisitos exigidos por la normativa andina (Decisión 486) vigente en nuestro país.

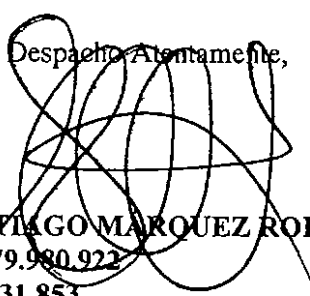
4. Anexos

- Copia simple de los documentos EP 1159877 (D1), WO 96/39855 (D2), US 2006/0051488 (D3).
- Copia simple del documento: “Towards a multidisciplinary approach to structuring in reduced saturated fat-based systems – a review”. Danisco 2010. (D4)

5. Notificaciones

Recibiré notificaciones en la Secretaría de este Despacho o en la Calle 98 No. 9-03 oficina 701.

De su Despacho Atentamente,



SANTIAGO MÁRQUEZ ROBLEDO
CC. 79.980.922
TP. 131.853



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
05.12.2001 Bulletin 2001/49

(51) Int Cl.7: **A23D 9/00, A23D 7/00,
C11B 7/00, C11C 3/10**

(21) Application number: 01202037.6

(22) Date of filing: 29.05.2001

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 29.05.2000 MY 0002388

(71) Applicant: Premium Vegetable Oils Berhad
50000 Kuala Lumpur (MY)

(72) Inventor: **Sahasranamam, Ulianoor Madam
Ramasubramaniam
80100 Johor Bahru (MY)**

(74) Representative: **Barendregt, Frank, Drs.
van Exter Polak & Charlouis B.V.,
P.O. Box 3241
2280 GE Rijswijk (NL)**

(54) **Trans free hard structural fat for margarine blend and spreads**

(57) A Trans free hard structural fat suitable for the manufacture of low SAFA (Saturated Fatty Acid) poly/mono unsaturated margarine and spreads and fat blends for margarine/spreads. The structural fat is made from selectively fractionated non-hydrogenated high

melting palm oil fraction which is interesterified with dry fractionated non hydrogenated palm kernel fraction with high yield ratios that can be economically and commercially used as structural fat for the aforesaid manufacture.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: EDIBLE PLASTIC SPREAD		
(57) Abstract		
An edible plastic spread is provided consisting of a continuous fatphase and optionally an aqueous phase wherein the fat of the fatphase includes at most 5 % trans-unsaturated fatty acid residue, consists of 40 - 90 % of liquid oil and 60 - 10 % of structuring fat which structuring fat comprises chemically unmodified palm oil or one or more palm oil fractions or a combination of 2 or more thereof, and includes hydrogenated and/or interesterified fat and/or animal fat such that the amount of interesterified fat is at most 70 % of the structuring fat, contains: at most X % symmetrical POP triglycerides or more than X % symmetrical POP triglycerides and contains asymmetrical PPO triglycerides such that $P20 \leq 16-4$ (POP/PPO) wherein P indicates palmitic acid residues, O indicates oleic acid residues, P20 indicates the sum of POP and PPO triglycerides and $X = 3.5$, and has an $N20 \geq 4.5$. In the product substantially no fat particles of a size visible with the naked eye develop upon storage for at least 3 weeks at 5 °C.		



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PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
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US 20060051488A1

(19) **United States**

(12) **Patent Application Publication** (10) Pub. No.: **US 2006/0051488 A1**
De Muijnck (43) Pub. Date: **Mar. 9, 2006**

(54) **LOW AND NO TRANS FAT CONFECTIONS**

Publication Classification

(76) Inventor: **Leanne De Muijnck, Milwaukee, IL**
(US)

(51) **Int. Cl.**

A23D 9/00 (2006.01)

(52) **U.S. Cl.** **426/607**

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(57)

ABSTRACT

(21) Appl. No.: **11/220,799**

(22) Filed: **Sep. 6, 2005**

Related U.S. Application Data

(60) Provisional application No. 60/607,773, filed on Sep. 7, 2004.

A fat composition for use in food products is provided, which contains low levels of trans fats, and includes a non-hydrogenated fractionated palm kernel oil and a non-hydrogenated fractionated palm oil. A confectionery composition containing the fat composition also is provided. The confectionery composition can be used to coat a food product, and can be flavored and/or colored. Methods for making a confectionery composition using the fat composition also are provided.



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ABSTRACT

(21) **Appl. No.:** 11/220,799

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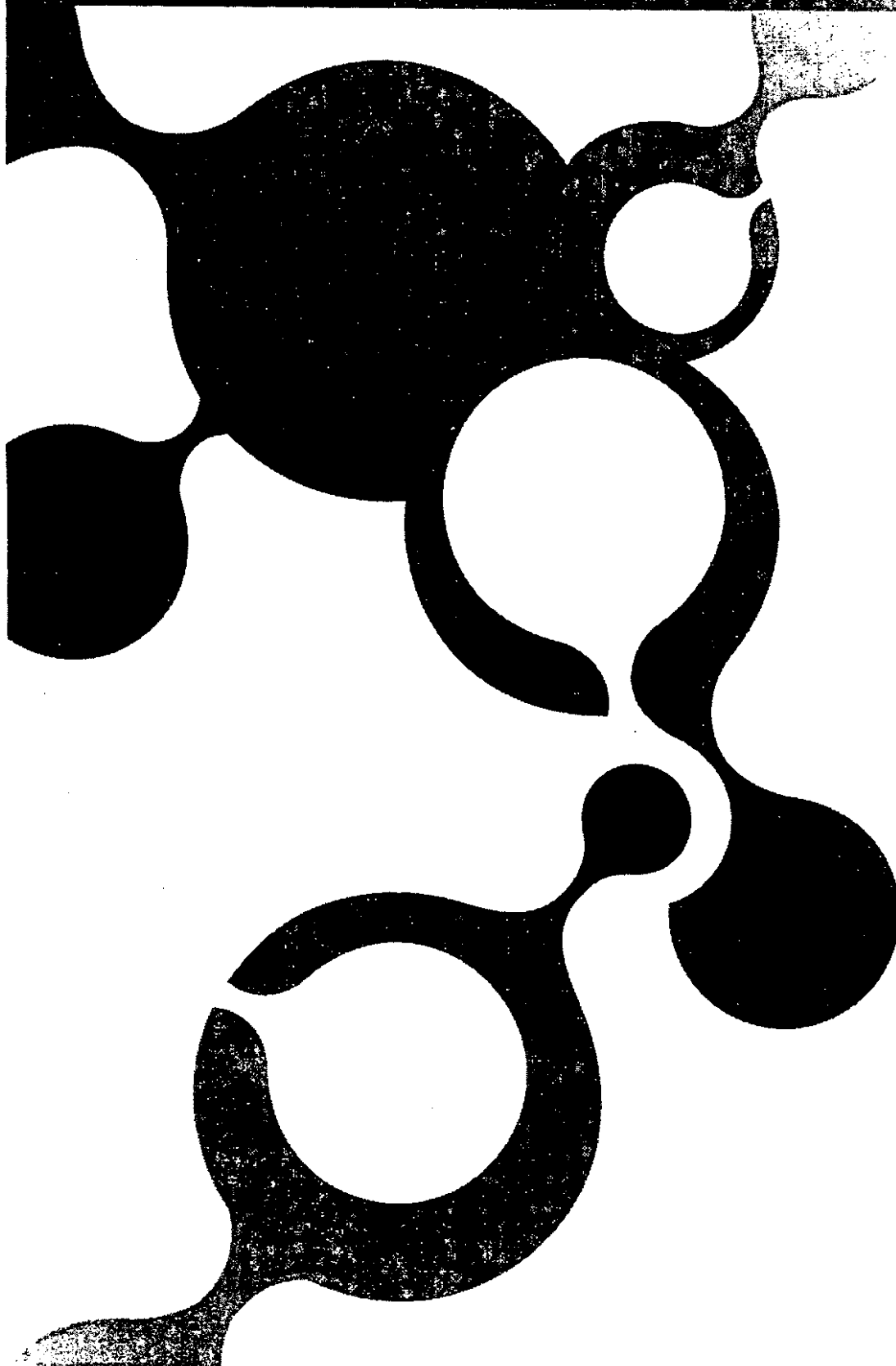
A fat composition for use in food products is provided, which contains low levels of trans fats, and includes a non-hydrogenated fractionated palm kernel oil and a non-hydrogenated fractionated palm oil. A confectionery composition containing the fat composition also is provided. The confectionery composition can be used to coat a food product, and can be flavored and/or colored. Methods for making a confectionery composition using the fat composition also are provided.

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Towards a multidisciplinary approach to structuring in reduced
saturated fat-based systems – a review

DANISCO



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SUMMARY

Although many food products are essentially emulsions, interest in the structuring of oil-continuous emulsions (and in specific cases water-continuous emulsions) is intense, particularly to meet the continuing challenge of reducing the degree of saturates in food systems. Consequently, it is necessary to observe the effects of structurants and to examine their impacts on current food systems. This is especially the case where novel structuring materials are used to wholly or partially replace traditional structurants. A multidisciplinary approach is discussed encompassing traditional and novel mechanisms considered able to structure within low saturated fat-based systems and which in themselves could also have emulsification properties. The presence of interfacial compositions as in emulsions requires a crucial understanding of the interactions within these compositions for the creation of building blocks in oil or fat structuring. Where a co-surfactant structure may be used, together with novel structurants, for example, wax esters, phytosterols, it is necessary to understand how these may influence interfacial film thickness, strength and flexibility. Understanding how to measure mechanical visco-elastic properties of structurant interactions both in model and real time dynamic measurements will be necessary to account for diffusion, orientation and self-assembly mechanisms.

This review discusses combining traditional techniques with novel structurant technology; developing and validating dynamic measurement techniques; and investigation of real systems as opposed to purely model systems.

INTRODUCTION

The issue of *trans* fatty acids (TFA) replacement has been the subject of intense discussion and debate within the food industry as well as in the clinical field, with

a strong focus on reducing total saturated fatty acid content for health reasons (Berger, 2009; Fletcher, 2006; FSA, 2008). Achieving this is not simple, because many consumers expect particular textural properties in a given food product. The aroma, texture and mouth sensations experienced when consuming these foods are strongly dependent on their fat content and can eventually shape dietary choices in the long term (Drewnowski *et al.*, 1989; Drewnowski & Almiron-Roig, 2009). Thus, the idea of reformulating familiar foods which historically contained significant amounts of fats and oils (and usually contain significant levels of saturated fat) into lower fat versions is challenging not only technologically but also from a consumer acceptance point of view. Research into consumer perceptions of a new food product is often compared with memorised experience from a similar consumed food. Consumers may tend to conclude their decisions on the basis of their memory of a food, and not on the basis of their actual perceptions (Mojet & Koster, 2005; Morin-Audebrand, 2009).

It is reported that the consumption of TFAs may raise low-density lipoprotein (LDL) cholesterol levels, and lower high-density lipoprotein (HDL) cholesterol levels, thus contributing to atherosclerosis and an increased risk of apoplexy (European Food Safety Authority, 2004; FSAI, 2008; Gidding *et al.*, 2009). However, there is still debate as to the relevance of the intake of TFA from naturally occurring ruminant sources (Willett & Mozaffarian, 2008) and of the importance of saturated fats. McNeill (2009) clearly showed that despite a large body of epidemiological data being generated over the last two decades in respect of their adverse effects, there are also apparently certain important positive effects. Thus the effects of saturated fats on cardiovascular disease are complex.

Legislation, and literature (Dubinsky, 2008; Mozaffarian *et al.*, 2006; Stender & Dyreberg, 2003; Stender *et al.*, 2006; WHO, 2007) state that *trans* fatty acids should be removed from food, but current research (Stender *et al.*, 2009) suggests that this is insufficient in terms of creating healthy foods. Removal of, or at least drastic reduction of, not only *trans* containing fats, but all saturated fats is also required (Merchant *et al.*, 2008; SACN, 2007; Wassell & Young, 2007; Young & Wassell, 2008).

Realising the legislative requirements of governments, and consumer expectations for the food industry, is a tremendous challenge (Pernetti *et al.*, 2007). Achieving this balance of adequate structure in fat-based food systems whilst lowering the total saturated fatty acid content is a major objective of the food ingredient industry which remains elusive. For well over a decade the issue of *trans* fatty acid removal from bulk fat based systems has been the main focus of research in this field (Wassell & Young, 2007), and in some countries remains so (Benincá *et al.*, 2009; Willson, 2009), for example, Brazil and USA, respectively. However, the predominant global attention is in reducing total saturated fats, which of course includes *trans* fats (FSAI, 2008; L'Abbé *et al.*, 2009; Rogers, 2009; Wassell, 2010; Willett & Mozaffarian, 2008; Willson, 2009; Young & Wassell, 2008). However, whilst the problem is global, for some cases in emerging economies, the degree of importance placed on providing food products with lower *trans* and saturated fats has taken lower priority (Pérez-Ferrer *et al.*, 2010). Whilst there is general agreement that total fat levels should be reduced, there is disagreement as to the best route (Montague-Jones, 2009). Talbot *et al.* (2007) advocate the use of saturated fats preferably from natural sources. Others agree suggesting for example, that movement to reduce dairy food consumption

(and hence saturated fatty acids) irrespective of the nature of the dairy product should be made with caution (German *et al.*, 2009; SACN, 2007). Marangoni (2007) suggests that the use of saturated fat in the absence of *trans* fats is not a solution. As a result, alternative mechanisms for providing structure without saturated and/or *trans* fats to allow edible oil structuring have found increasing attention (Bot *et al.*, 2009b; Hughes *et al.*, 2009; Rogers, 2009).

Recent studies explore the different strategies including lipid crystal engineering (Schaink *et al.*, 2007); phytosterol systems (Bot *et al.*, 2009b); organogel-based emulsion systems (Duffy *et al.*, 2009) and wax technology to form "lipo-colloid" structures (Shigemitsu, 2006). A comprehensive discussion of current possibilities is proposed by Pernet *et al.* (2007), who state succinctly that finding alternatives to traditional triacylglyceride (TAG) structuring whilst maintaining healthy properties, versatility and performance, is a tremendous challenge.

The aim of this review is to highlight the current state of the art, and propose a multidisciplinary-based approach to achieving the goal of providing structure for low saturated TAG systems and characterising these by means of new analytical approaches, which may include measurements within both static (Anima *et al.*, 2009; Tanaka *et al.*, 2009) and dynamic conditions (Wassell & Young, 2007; Young *et al.*, 2008; Wassell *et al.*, 2010).

TAG STRUCTURING

Traditionally, where TAG structuring is used, hard fractions and/or modified hard stocks composed largely of saturated fatty acids, also contained significant amounts of *trans* isomers (Kodali, 2005; Flöter & van Duijn, 2006; Podmore, 2008; Wassell, 2010).

Modification techniques and even the simple selection of alternative oils, for example, rice bran oil, shea, moringa, allanblackia (Lalas & Tsaknis, 2002; Most *et al.*, 2005; Garcia, 2006; Ghosh, 2007), have demonstrated the possibility of minimising and controlling the *trans*/saturated content

of oil blends and to successfully formulate alternative hardstocks (Abdulkarim *et al.*, 2005; ACNFP, 2006; Bell *et al.*, 2007; Annon, 2008; MacKenzie, 2008; Lerma-García *et al.*, 2009; Mayamol *et al.*, 2009).

The combination of techniques leads to a greater variety of hardstocks with a wider range of physical properties such as solid fat content and melting profile. This is particularly important for fats from which a specific performance is expected. Exclusive focus on the physico-chemical aspects but neglecting the fat's required functional role within the final application leads to other problems. Matching the physical properties of a commercial fat blend to a specific application is normally based on solid fat profile, melting point and textural qualities. Subsequently, the commercial fat blend's plastic range might be expected to be within a given tolerance (Young & Wassell, 2007; Wassell, 2010). Ultimately, the reason for this is to fulfil performance phenomena such as creaming, crystallisation and emulsification, which also need to be considered. Therefore, fatty acid composition, polymorphism and process conditions can not be ignored. Concentrating exclusively on the fat phase does not necessarily address the whole challenge in the case of reducing total saturates, for example, addition of a water phase, creating an emulsion, which automatically reduces the fat content in the final application. However, to effectively pursue this strategy often requires balanced emulsifier technology and possibly the use of other additives, and even subsequent redesign of the final food product may be necessary (Wassell & Young, 2007). It is known that the composition, polymorphism, solid fat content and microstructure of TAGs all play a crucial role in the structure of lipid-based products (Christie, 1982; Timms, 1985; Garti & Sato, 1988; Larsson, 1994; Narine & Marangoni, 1999; Hartel, 2001; Rogers, 2009). The major advantage of TAG structuring is the diversity of the molecules and molecular configurations, which allows for the physical properties to be tailored to the final application by changing the chemistry of the molecules or by modifying the processing conditions,

enabling production of solid and semi-solid fats (Bailey's, 2005; O'Brien, 2009).

HYDROGENATION

Hydrogenation or partial hydrogenation processes, which have been commonly used in the modification of oils for food product formulations, are able to deliver specific, desired melting behaviours for fat blends (Hamm & Hamilton, 2000; Gunstone, 2002; Podmore, 2008; Dijkstra, 2009). The proportion of fatty acids which can be changed through hydrogenation is classified as unsaturated fatty acids, having one (monounsaturated), two or three (polyunsaturated) double bonds. These types of fatty acids usually have the *cis* configuration, that is, the hydrogen atoms with respect to the double bond are on the same side of the molecule. Fully saturated fatty acids do not contain double bonds and are least reactive chemically (O'Brien, 2009).

Addition of hydrogen atoms across the unsaturated double bonds, causing saturation of the TAGs, causes more rigid structures because of the new molecular configurations. Apart from removing or shifting the double bond, the same process can also cause the *trans* configuration associated with negative health effects (Stender & Dyreberg, 2003). Fatty acids specified as being in the *trans* configuration have the hydrogen atoms on the opposite sides of the molecule, and the molecule assumes a nearly linear configuration similar to saturated fatty acids. Hence *trans* fats behave more like saturated fatty acids. Partial hydrogenation, which is carried out to alter the plasticity and functional properties of a fat, produces several *cis* and *trans* fatty acids from intramolecular rearrangements. Irrespectively, any increase in saturation results in higher melting point of the TAG, and therefore, is more solid at room temperature (Foster *et al.*, 2009). Importantly, as mentioned during the introduction, not all *trans* fatty acids are produced by commercial hydrogenation (SACN, 2007; German *et al.*, 2009). Indeed there is intense debate where dairy fats are concerned and a need to differentiate between effects of hydrogenated and naturally occurring *trans* fats (Kummerow,

2009). Options to reduce the *trans* levels during the hydrogenation process of edible oil have been investigated (Beers, 2007).

INTERESTERIFICATION

In view of the limited ability of solidifying "natural" TAGs to create certain structures, other naturally occurring hardstock components, that is, from palm oil are used. The basic principles of interesterification were first documented by Fondu & Willems (1969) and they described a process which resulted in the rearrangement of the distribution of the fatty acids either chemically or enzymatically, within and between the triglycerides. Consequently, the fatty acid distribution is altered but the fatty acid composition remains unchanged – this rearrangement can occur either in a random or controlled manner (Yusoff & Dian, 1995). The net effect of rearrangement leads to production of oils that require a certain semi-solid-plastic range having different levels of structure, each influencing the macroscopic properties of the material (Tang & Marangoni, 2006a; Ribeiro *et al.*, 2009).

FRACTIONATION

The controlled crystallisation of TAGs can result in the separation (fractionation) of a solid phase (stearin) and a liquid phase (olein). In turn, these can be further fractionated (van Duijn *et al.*, 2006).

Essentially, the process of fractionation consists of crystallisation to produce solid crystals in a liquid matrix, and separation of the crystals from the liquid matrix (Timms, 1997). Fundamentally, fractionation processes work to the following principles: complete melting of the fat, slow cooling, gentle or no agitation to encourage the development of large crystals and separation into liquid and solid fractions with differing physical and chemical compositions (Timms, 2005). An excellent review by Timms (2005) discusses the different fractionation methods, and Dijkstra (2009) provides information on recent developments not just in fractionation, but reviews edible oil processing generally.

Palm is probably the most important oil in terms of fractionation because of its

unique fat profile (Sahasranamam, 2005) which can be broken down into individual fractions (Timms, 2007). Another term used for fractionation is winterisation, and is essentially the process of removing wax esters and high melting TAGs at lower ambient temperatures, and still has modern use today particularly for oils liquid in the ambient temperature range (MacKenzie, 2008).

Fractionation has been shown to be useful in the replacement of some emulsifiers – specifically highly saturated emulsifiers, with low iodine values, which are difficult to replace with non-hydrogenated emulsifiers. To supply emulsifiers, which have the same physical/chemical characteristics as the widely used hydrogenated types, but preferably, in a non-hydrogenated form is challenging.

It is the more saturated, and preferably the fully saturated monoglycerides which are able to assist in both emulsification and promote crystallisation. An example is in the preparation of emulsions for industrial margarines, which typically require use of simple monodiglycerides. Bech *et al.* (2008) describe a method of preparing a non-hydrogenated emulsifier having substantially no *trans* carbon-carbon double bonds, and further discusses other surfactants which are built on "natural"

feed stocks, which may be fractionated, to give remarkably low iodine values; an indicator of the degree of saturation.

Talbot *et al.* (2007) favour fractionation for design and control of the fat blend due to it containing a significant portion of high melting TAG's (Lida & Ali, 1998; Sundram, 2005). Timms (2005) neatly summarises the whole mechanism and comments that with the decline in hydrogenation, interesterification has seen a renaissance, although it is only partially able to replace hydrogenation. Additionally, interesterification suffers from the "chemical"-process image and environmental drawbacks of hydrogenation. Therefore, fractionation, a purely physical process, more adequately satisfies today's increasing environmental and health concerns.

NON-TRADITIONAL STRUCTURANTS

As TAGs are responsible for the network structure in traditional systems, it is difficult to entirely remove saturated fats without compromising some sensory and physical characteristics. Alternative structurants for discussion are listed in figure 1. Several reviewers acknowledge the necessity to revisit some of the traditional solutions and couple these with the use of novel materials, because it is unlikely that one novel structurant, for example, mixture

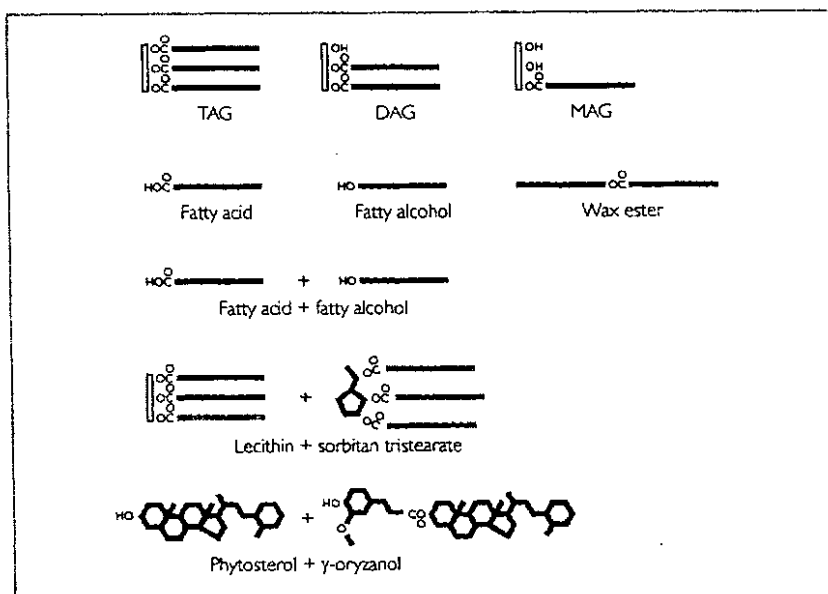


Figure 1. Schematic representation of a number of structurants for TAG oil phases (Pernetti *et al.*, 2007).

of phytosterols and oryzanol could satisfy all requirements. Rather, this mixture in a TAG-based, water-in-oil emulsion with a surfactant is more realistic (Pernetti *et al.*, 2007; Schaink *et al.*, 2007; Bot *et al.*, 2009b). Therefore, textural properties to which consumers are accustomed may not be achieved through singular techniques. It is likely that synergies obtained through combining disciplines, understanding of thermodynamic mechanical properties and critical design of real systems, will play a vital influence (Fomuso & Akoh, 2001; Pernetti *et al.*, 2007; Duffy *et al.*, 2009; Hughes *et al.*, 2009; Rogers, 2009). Therefore, it is suggested that a multidisciplinary approach to the study, design and possible solution of the problem is necessary (Wassell & Young, 2007; Young *et al.*, 2008; Wassell, 2010).

TAG

Apart from that discussed in the TAG structuring section, Higaki *et al.* (2003) observed gel-like behaviour in TAG mixtures of fully hydrogenated rapeseed oil with behenic acid concentrations of 1.5–4.0 wt%. Rapid cooling and heating to final temperature were necessary to achieve gel-like behaviour, whereas simple cooling without a cooling/heating procedure did not form a gellike fat mixture. This is attributed to cooling rate, agitation and degree of supercooling, control the rate of crystal growth and thus crystal size and crystal agglomeration, which affect the textural and melting properties of the fat product (Humphrey & Narine, 2004). Importantly, Higaki *et al.* (2003) was able to influence polymorphism by adjusting thermal treatment and tempering, to achieve a β -gel without waxes, or other emulsifier additives. The subject of polymorphism is not discussed in any detail within this review, and good explanations are provided within the literature (Hernqvist, 1984; Sato, 2001).

Mentioned in the previous section, Pernetti *et al.* (2007) discusses several mixed structurant systems could benefit from utilising TAGs with novel structurants under specific process conditions, a multidisciplinary approach. This will subsequently be enlarged upon during this discussion

(Wassell & Young, 2007; Young *et al.*, 2008; Hughes *et al.*, 2009; Wassell, 2010).

DAG

Pernetti *et al.* (2007) note that surprisingly little attention has been given to structuring using diacylglyceride (DAG or diglyceride), and the authors cite dipalmitin and distearin as forming crystalline networks in a similar way to those formed by TAGs. These gel formations are slightly softer than TAG crystal networks of similar concentration. Indirectly, the reduction and influence of diglyceride content can also play a positive effect as a β -l stabiliser (Hernqvist & Anjou, 1983; Cheong *et al.*, 2009), which has not really been exploited (Kristensen *et al.*, 2005). The reduction of diglycerides in palm oil rich blends, can lead to an increase in the total solid fat content. Thus, it is possible to produce similar viscoelastic profiles in products, normally associated with a higher degree of saturated fatty acids. Examples are: margarine, salad dressing products, nutritional bars, muffins, brownies, breads, cookies, doughs and batters for baked goods (Boice *et al.*, 2003; Sikorski, 2005; Kristensen & Wassell, 2006).

MAG

Monoacylglycerol (MAG or monoglyceride) components are able to structure both lipid and aqueous phases (Marangoni, 2007; Rogers, 2009; Rush *et al.*, 2009). MAGs are thought to form reversed bilayers in TAG oils. Ojijo *et al.* (2004a,b) investigated the formation of stable network structures through the cooling of mixtures of various concentrations of monoglycerides and vegetable oils. Mechanical hardness of olive oil/MAG gel networks was investigated. A given minimum monoglyceride volume fraction was necessary for formation of a gelled network. The onset of the gel network or structure formation was indicated by a change in the value of the elastic modulus, whilst network hardness increased with increase in MAG content. High cooling rates led to low final elastic modulus values but harder networks, whereas slow cooling rates gave the reverse. Maximum gel network development occurred with moderate shear rates, thereby highlighting

the fact that the physical and functional characteristics of such products, in this case, depend on processing conditions, cooling rate, shear and presence of co-surfactants (Ojijo *et al.*, 2004b; Pernetti *et al.*, 2007; Davis *et al.*, 2009; Hughes *et al.*, 2009; Krabbenhoft *et al.*, 2009; Rogers, 2009; Tippetts & Martini, 2009).

Novel structurants

Hughes *et al.* (2009) report that a number of organogelator systems have the ability to gel edible oils at very low concentrations (~0.5–2.0 wt%), and apart from those previously mentioned, include network-forming edible oil structurants: TAGs, DAGs, MAGs. Murdan *et al.* (1999) discuss sorbitan mono-stearate and Gandolfo *et al.* (2004) and Schaink *et al.* (2007) discuss mixtures of fatty acids and fatty alcohols. Combinations of lecithin and sorbitan tri-stearate, phytosterols and oryzanol have also been reviewed (Pernetti *et al.*, 2007). Other organogelators or mixtures are well-known for their ability to structure in edible oils: 12-hydroxystearic acid (Rogers *et al.*, 2007, 2008a,b, 2009), ricinelaidic acid (Wright & Marangoni, 2006), candelilla wax (Toro-Vazquez *et al.*, 2007), mixtures of β -sitosterol and γ -oryzanol (Bot & Agterof, 2006). Rogers *et al.* (2009) also show that sphingolipids, like triacylglycerides, can exhibit variability in the fatty acid chain length. These are able to form long thin fibre structures, creating greater surface area and thereby stabilising more polyunsaturated liquid oil (Christie, 2010).

Irrespective of the network composition, organogels have numerous potential different functionalities in food products (Duffy *et al.*, 2009), and are not limited to oil mobility and migration, the replacement of saturated and *trans* fats, and the stabilisation of emulsions (Pernetti *et al.*, 2007; Rogers, 2009). Network forming modified polymers are known to have dual affect as structurant and surfactant capability at oil water interfaces, but these are usually non-edible applications, and therefore not within the scope of this review.

Other food grade polymers include cellulose derivatives including chitosan (Pszczola, 2006; Rietberg & Marangoni,

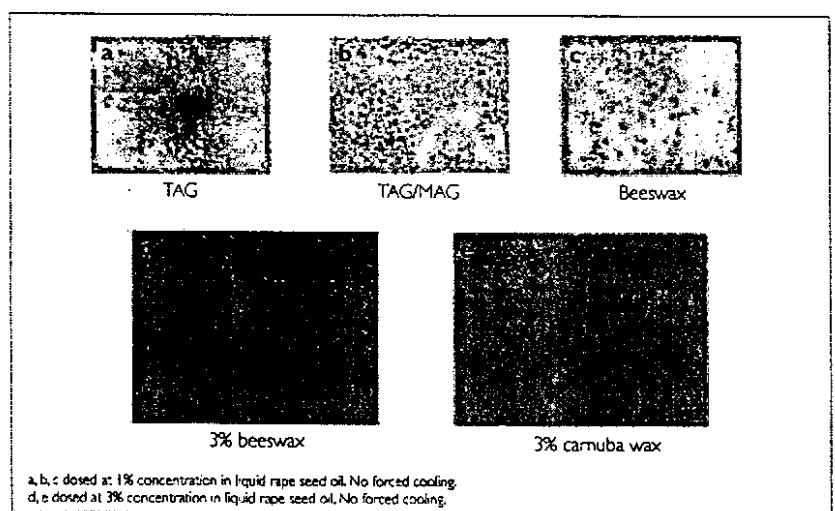


Figure 2. Waxes compared with traditional TAG and monoglyceride (MAG) (M. Nielsen, unpublished data).

2009), however, the use of these materials for edible oil structuring is rare due to restrictions on modifications for food use (Pernetti *et al.*, 2007) and therefore applications tend to be associated to oil-in-water applications because cellulose derivatives such as cyclodextrins must be fully hydrated for functionality (Cui & Wang, 2006).

Waxes/fatty acids/phytosterols
Experimental application of wax in peanut butter provides an example of a multidisciplinary approach, where a naturally slow crystallising beeswax is used to replace traditional TAG based hardstock. A "lipocolloid" – like network is formed, with efficient needle shaped structures, rather than spherical shaped particles (Pernetti *et al.*, 2007). Waxes compared with traditional TAG and MAG solutions are shown in figure 2. In liquid oil, similar yield stress values can be achieved using lower inclusions than typical TAG or MAG concentrations (M. Nielsen, unpublished data). Mellema (2009) studied co-crystallisation of beeswax and various vegetable waxes with sterols and reported that rice bran wax, sunflower wax and jojoba can increase crystal events in a formulation. Furthermore, Mellema (2009) highlighted the benefits of heRP70 (fatty acid composition: C16:0–5%, C18:0–40%, C20:0–9%, C22:0–43% with more than 99.5% total saturated fats), reporting the replacement of beeswax with combina-

tions of heRP70, sunflower oil, or jojoba wax also significantly increased the amount of crystalline material in the formulation. This was attributed to improved solubility of the sterols. This provides scope for combining traditional and novel solutions (Pernetti *et al.*, 2007). Toro-Vazquez *et al.* (2007) established the oil structuring property of candelilla wax in safflower oil at concentrations of ~1 wt% and higher. Kodali (2009) also reports Ricebran wax being able to stabilise other long chain polyunsaturated oils.

Dassanayake *et al.* (2009) report network formation of rice bran wax crystals and show organogel properties occurred more rapidly, coinciding with temperatures of crystallisation than that of the mixtures of carnauba wax and candelilla wax in olive oil. The same authors also observed a low concentration of carnauba and candelilla wax was necessary to form an organogel in olive oil at 4 and 2 wt%, respectively. Gel structures formed soon after rice bran wax crystallised, whereas a time delay was observed between the organogel formation and wax crystallisation of carnauba wax and candelilla wax, demonstrating rice bran wax has good organogelforming properties. The quicker gelation in the rice bran wax system was attributed to comparatively longer fibrous crystals of rice bran wax which form gelator networks efficiently entraining the liquid oil.

Martini *et al.* (2008) discuss two different crystal populations when testing sunflower oil wax (SFOw) in anhydrous milk fats (AMF) and suggest the presence of two different populations of crystals. This could be attributed to differences in the molecular weights of SFOw and AMF, where the AMF at high temperatures crystallise very slowly forming large agglomerates. These authors found that the addition of SFOw could decrease the induction time of crystallisation, promoting crystallisation, especially towards high temperatures. Dassanayake *et al.* (2009) reported the presence of different components within the wax, which seemed to have a profound effect on the crystal habit of the plant wax–vegetable oil organogels. Conditions of organogel preparation (e.g. degree of agitation, cooling rates and storage conditions) were likely to influence crystal morphology of the gelators.

Mellema (2009) investigated methods for solubilising sterols, which in themselves form structures, but can be difficult to incorporate into TAG systems (Pernetti *et al.*, 2007; Hughes *et al.*, 2009; Rogers, 2009). Mellema (2009) found that mixing molecularly similar waxes, including ursolic acid (found within apple waste) facilitated the incorporation of sterols. Bhaggan *et al.* (2002) showed that by adding a blend of ursolic acid and oleanolic acid to a fat *per se* or to a fat in a food product, the crystallisation rate of the fat could be increased concomitantly with the hardness of the fat composition. Furthermore, it was found that the addition of the ursolic acid/oleanolic acid mixture also improved other properties of the total composition, such as oral mouthfeel, heat resistance, and aeration properties. Combining waxes and specific fatty acids, might be suitable, because of their similar hydrophobicity to sterols and their typical plasticity, which allows a structural "flexibility" for the sterols to fit into a crystal network (Mellema, 2009).

Organogel – phytosterol emulsions/ 12-hydroxystearic acid
Little is known about the structures formed in specific organogels and how these structures might behave at the emul-

sion interface. Duffy *et al.* (2009) studied oil-in-water organogels based on edible oils and specific mixtures of phytosterols, in an attempt to describe and understand micro-structural features, prepared using basic processing conditions. They showed that long thin crystals are formed extending out of the oil phase into the continuous water phase. These emulsions of phytosterol-based organogels in an aqueous solution formed with the presence of emulsifiers and resulted in the formation of small emulsion droplets; internal oil droplet structure was not studied. Schaink *et al.* (2007) showed that lipid crystal engineering using mixed crystals offers the prospect of obtaining harder organogels with less structurant. A possible application of this type of structurant mixture is the replacement of saturated fats in a broad range of water-in-oil products. For these applications, it is important to know whether the mixed crystals also contribute to the visco-elastic properties of W/O and O/W emulsions that are made using these structurants. Observing and explaining these effects is of technical relevance and should be investigated. Schaink *et al.* (2007) suggested that it would be interesting to combine different approaches in order to obtain an insight into the mechanism of organogel formation, which may lead to improved understanding of the polymorphism and crystal formations resulting from mixed components. Ishizuka *et al.* (2009) reported that surfactant

molecules in water and other solvents can form various self-assembled structures such as micelles and liquid crystals, because of their hydrophobic interaction. The micellar shapes can vary from spherical to worm-like structures, depending on composition, temperature and other factors. When micelles grow to form aggregates and behave like polymers, becoming highly visco-elastic, they may entangle each other.

"Self-assembled fibre networks" (SAFiN) are well reported (Pernetti *et al.*, 2007; Rogers *et al.*, 2008a; Rogers, 2009) and spontaneously form fibres, capable of structuring the oil phase. Duffy *et al.* (2009) report systems able to form structure in the aqueous phase, and it has been confirmed (Bot & Agterof, 2006; Bot *et al.*, 2008; 2009a) that β -sitosterol – γ -oryzanol fibril systems are quite unique as they are one of the few combinations capable of forming fibril structures in both aqueous and oil systems. Both Duffy *et al.* (2009) and Ishizuka *et al.* (2009) report formation of micellar tube-like structures (figure 3) in the aqueous phase. They found their formation to be time and temperature dependent and they concluded that a diffusion-based mechanism might occur, in which the sterols or sterol containing features move and rearrange from the lipid phase into the aqueous phase. Duffy *et al.* (2009) show that sterol solubility in edible oil is further reduced with the transition from a pure organogel system

to an organogel- based emulsion system, and explained that in hot dry vegetable oils sterols are reasonably soluble, but this decreases in oil saturated with water (Jandacek *et al.*, 1977; Duffy *et al.*, 2009). This has implications, because depending on the presence of another co-structuring material, for example, lipid; it may affect diffusion, and integration kinetics differently (Povey *et al.*, 2007).

The above observations have significance not only to the understanding of how these structurants are behaving in model systems but also to their behaviour in "real" emulsions. This raises the question of how combinations of such structurants may perform both thermodynamically and mechanically at the interfaces of O/W or W/O emulsions (Bot *et al.*, 2009a,b). Thus the question of phytosterol solubility and its potential structuring ability requires further investigation. Understanding how to measure mechanical visco-elastic properties of structurant interactions both in model and real time dynamic measurements (Povey *et al.*, 2007; Ishizuka *et al.*, 2009; Ojijo *et al.*, 2009) will therefore become increasingly necessary (Pernetti *et al.*, 2007; Schaink *et al.*, 2007; Arima *et al.*, 2009; Rogers, 2009; Tanaka *et al.*, 2009; Young *et al.*, 2008).

Application of alpha (α) polymorphic tending emulsifiers (Stauffer, 1999) in liquid vegetable oil to form a soft gel mixed into the aqueous phase has been reported (Wassell, 2006a,b). The α crystalline form is more flexible than the rigid beta (β) crystalline form and rearranges more easily during heating cycles. The former establish a physical film at the interface of the oil droplets and prevent inhibition of foam formation with relatively low levels of total oil/solid fat. This provides a significant reduction of total saturates (Wassell & Young, 2007). A suppression of the solid fat content is also observed with additions of between 5 and 10 wt% mixed, fully hydrogenated surfactants (Wassell, 2006a,b). Suppression, and time delay of solid fat content is also reported by Hughes *et al.* (2009) where addition of 2% w/w 12-hydroxystearic acid (12-HSA) to a model filling (60:40 canola

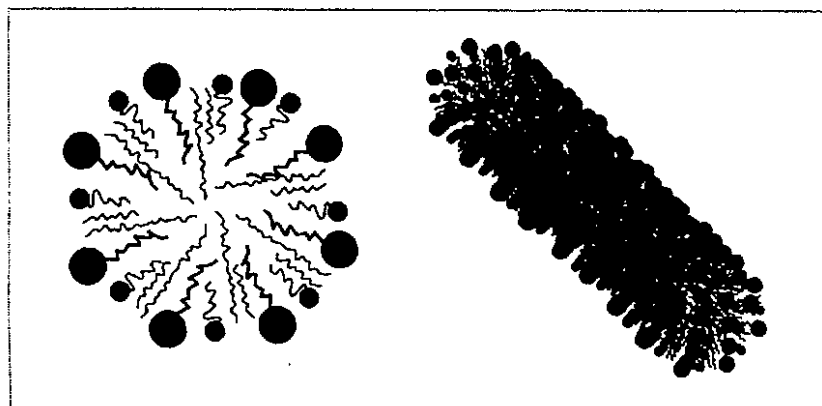


Figure 3. Schematic diagram (hypothetic model) of the ordering of the two sterol species with triacylglycerides in a 10-nm tube structure. The molecules are drawn on scale approximately. Red γ -oryzanol, green β -sitosterol; "chair-model": triacylglycerides. The right image shows a schematic diagram of the tube structure; organisation of the sterols with respect to each other may be more random. Adapted from Duffy *et al.* (2009).

oil: interesterified hydrogenated palm oil) composite cream-filled confection, did not increase the solid fat content of the mixture. Isothermal crystallisation occurred at 20 °C. The authors explained that 12-HSA is a high melting point lipid component, and therefore, theoretically the SFC of the mixture would be expected to increase proportionally with its addition. However, its inclusion did not translate to a higher SFC and therefore addition of 12-HSA either delays or slows normal crystallisation (Hughes *et al.*, 2009).

Hughes *et al.* (2009) proposes potential food applications of edible oil organogels and emulsions, reporting the complexity of network formation and bonding interactions, and is considered difficult to design systems or predict which organogelators will work with a particular solvent, therefore immobilised water droplets within a continuous gelled oil phase were investigated. Hughes *et al.* (2009) suggest that given certain formulation and processing conditions, organogelled emulsions may have application as low-fat spreads or to control the release of both hydrophilic and hydrophobic bioactive (probiotic) compounds (Hughes *et al.*, 2009).

Hughes *et al.* (2009) report the potential application of water-in-gelled-oil emulsions, where addition of typical food grade emulsifiers (i.e. Span 60 or Tween 80) drastically modified the textural properties which can negatively affect the ability of 12-HSA to gel oil. 12-HSA is not considered a food grade additive as it is derived from castor oil and is considered an irritant, although Rogers (2009) reports it as being an ideal compound for examining macroscopic changes in processing conditions. Others have recently investigated and studied the physico-chemical, self-assembling behaviour and potential of 12-HSA, to form tube like structures. Additions in excess of 30% of other lipids (saturated fatty acids), or phospholipids could be incorporated without negatively affecting structure (Fameau *et al.*, 2010).

Crystal habit modifiers and co-gelators

Recent publications have discussed the use of "crystal structure modifiers" (Garbolino

et al., 2005; Rousseau *et al.*, 2005; Pernetti *et al.*, 2007; Young *et al.*, 2008), addition of a co-surfactant (Foster *et al.*, 2007; Rogers, 2009), inclusion of an additive, accelerant (Katsuragi, 1999; Fujiwara *et al.*, 2000; Wassell *et al.*, 2010), or impurity (Awad & Sato, 2001, 2002).

Crystal structure modifiers are potentially interesting not only within traditional systems, but also within novel structures and mixtures (Pernetti *et al.*, 2007). Effects of, hydrophobic, adsorption properties of additives and template behaviour for acceleration of surface heterogeneous nucleation events have been studied (Awad & Sato, 2001, 2002; Cerdeira *et al.*, 2003, 2005, 2006; Sakamoto *et al.*, 2003, 2004). More recently, the behaviour of unsaturated and saturated surfactants, their polymorphism, time temperature effects and advanced analysis (Arima *et al.*, 2009; Tanaka *et al.*, 2009) has provided information on the interactions of minor components (Vereecken *et al.*, 2009a) and crystallisation with and without water phase (Vereecken *et al.*, 2009b). Whilst all these observations are vital in providing understanding, it is also considered important to observe effects of mixed surfactant systems, and how these interactions influence their relative relationship in TAG and non-TAG mixtures (Pernetti *et al.*, 2007; Rogers, 2009). Investigation of the kinetic stabilisation of emulsions with low concentrations of continuous phase crystals (Rousseau *et al.*, 2005) found polymorphic form and morphology could be manipulated through a multidisciplinary approach, involving dilution, tempering regime and the presence of polyglycerol polyricinoleate (PGPR), under different crystallisation conditions – this being static vs. dynamic crystallisation (Young *et al.*, 2008; Wassell *et al.*, 2010). Rousseau *et al.* (2005) suggest liquid emulsifiers such as PGPR compared with surfactants such as saturated MAG are not as likely to influence crystal lattices, unless PGPR is combined with agitation conditions, where polymorphic transformation was retarded. However, static crystallisation in the presence of PGPR showed no differences. This aspect could be especially interesting to observe in the area of high internal-phase-

ratio emulsions (HIPREs) (Charteris, 2007) where interfacial film strength and mechanical flexibility will probably impact on final structures resultant from adsorption, diffusion and integration kinetics (Povey *et al.*, 2007).

Attempting to modify structures based on traditional, novel or a combination of these approaches, and especially where thermodynamic conditions are combined with co-gelators such as mixed surfactants, could lead to some potentially interesting physical properties (Hughes *et al.*, 2009; Rogers, 2009). Recently Bot *et al.* (2009b) investigated the importance of the composition of emulsions based on β -sitosterol and γ -oryzanol and found that increases in phytosterols led to an increase in firmness of the emulsion gel and that changing the ratio of β -sitosterol to γ -oryzanol proved more sensitive than previously observed for the pure organogels (Bot & Agterof, 2006). Bot *et al.* (2009b) also found it more critical to use a 40:60 β -sitosterol to γ -oryzanol weight ratio in order to achieve the optimal emulsion firmness. The effects of a number of minor ingredients, including MAGs, and make up of the water phase, were also investigated. The authors concluded that water activity is not important for the emulsion's properties, and found the addition of MAGs reduced droplet size and improved spreadability (Ritter *et al.*, 2005). Bot *et al.* (2009b) speculated that smaller droplets cause smaller "defects" in the organogel network, leading to firmer emulsion gels, but seem to be sensitive to the combination of cooling and shearing normally used in W/O emulsion processes. Hughes *et al.* (2009) found similar challenges when investigating organogel emulsions based on 12-HSA, though ultimately finding 12-HSA crystals to be dispersed evenly throughout the continuous oil phase and were not present inside or concentrated at the surface of the water droplets. Fairly large water droplets were formed, but these were stable (Hughes *et al.*, 2009). Both examples from Bot *et al.* (2009b) and Hughes *et al.* (2009) highlight room for further improvement in the emulsion preparation process. Research from studies within other disciplines (Peng *et al.*, 2009) may provide clues to the

formation of HIPREs using cholesterol derivatives as natural emulsifiers. HIPREs emulsions contain an internal phase volume of 70% (v/v) or greater, forming dispersed polyhedral structures, separated by thin films of continuous phase. These highly concentrated emulsions are also called "gel-emulsions" because of their visco-elastic behaviour (Peng *et al.*, 2009).

TECHNIQUES FOR INVESTIGATION

Most studies have been performed under isothermal conditions where observation of crystal behaviour is potentially quite different from that observed within a dynamic environment (Garbolino *et al.*, 2005; Janssen & MacGibbon, 2007; Maleky *et al.*, 2007; Povey *et al.*, 2007; Wassell *et al.*, 2010). Interactions of and between surfactants and their interactions as template structures, for example, in heterogeneous nucleation events (Fujiwara *et al.*, 2000), are not easily explained with typical measurements such as rate of crystallisation tests – static conditions – zero shear, and synchrotron (X-ray/DSC) tests – static conditions – zero shear (De Graef *et al.*, 2006; Pemeti *et al.*, 2007; Povey *et al.*, 2007). Improved understanding may therefore require the use of new techniques capable of observing and quantifying structural events in both static and under dynamic conditions (van Duynhoven *et al.*, 2005; Tang & Marangoni, 2006b; Arima *et al.*, 2009; Boodhoo *et al.*, 2009) and describing this relationship to their me-

chanical properties, for example, ultrasonic velocity profiling with pressure difference (UVP-PD) equipment allowing non-invasive in-line rheological measurement and synchrotron radiation microbeam small-angle XRD (SR- μ -SAXD) technique to more precisely observe microstructures of fat crystals (Prakash & Ramana, 2003; Mazzanti *et al.*, 2005; De Graef *et al.*, 2006; Maleky *et al.*, 2007; Pemeti *et al.*, 2007; Young *et al.*, 2008; Tanaka *et al.*, 2009; Wassell *et al.*, 2010). Determination and validation of methods will of course have to be approached with caution, in order to obtain an understanding of the potential diffusion or self organising mechanical properties leading to achievement of clear rheological behaviours (Morales-Rueda *et al.*, 2009). Nucleation events, which are likely to be heavily influenced by small quantities of high melting fats, acting as seed crystals, may be difficult to establish with current analytical techniques. The surface integration of molecules into growing crystals can similarly be upset by small quantities of impurities. Further, where fat crystallisation occurs within emulsions, this introduces additional complications (Himawan *et al.*, 2006).

DISCUSSION

Two themes seem to run through the literature; first, the necessity to move away from the addition of hard fatty material and substitute by alternative structure forming strategies. Second (related to first theme) is the need to

cause accelerated nucleation events through inclusion of a small amount of additive such as a surfactant. Such technology is well documented (Sakamoto *et al.*, 2003, 2004) and commercialised (Neddersen *et al.*, 2009). Therefore, given the aforementioned approaches, there are two areas for consideration; not just structure and assembly within the bulk oil, but the mechanism of structure at interfaces, for example, water-in-oil emulsions, and how the interface might be modified through surfactant-initiated surface heterogeneous nucleation to provide adequate structure, strength, and flexibility through a range of mechanisms (Povey *et al.*, 2007).

It is probable that there is a mechanism which could employ the use of "traditional" TAG-based structurants, coupled with novel structuring types (Pemeti *et al.*, 2007; Duffy *et al.*, 2009). For example, one of a range of previously discussed assemblies might be more efficiently optimised over shorter induction times, as a result of the inclusion of a material acting as an accelerant which might otherwise have been considered an impurity (Wassell *et al.*, 2010).

Structurants such as γ -oryzanol which work very well in bulk oil, may have limits within water-in-oil emulsions for products such as spreads, as they cannot provide the textural properties consumers are familiar with. However, modification of the thermodynamic driving force and addition

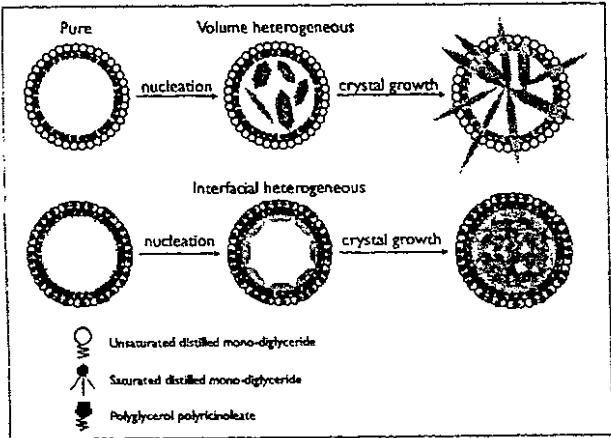


Figure 4. Heterogeneous crystallisation of O/W emulsion with additive. Adapted from Arima *et al.* (2007).

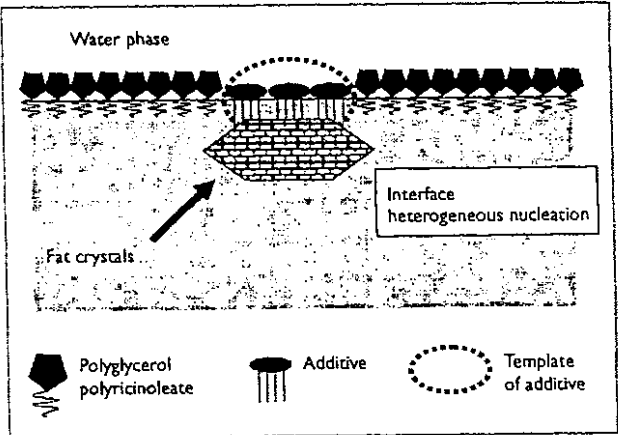


Figure 5. Additive to induce crystal nucleation, whilst retarding crystal growth. Adapted from Sato (2005).

of a co-surfactant (Foster *et al.*, 2007; Pernetti *et al.*, 2007; Rogers, 2009) could achieve nucleation through standard accelerated induction events with inclusion of a surfactant, for example, monoglyceride.

Among the components discussed by Rogers (2009), fatty acids, particularly long chain fatty acids, are ignored due to the negative health implications associated with traditional fat based networks. However, whilst the use of saturated TAG networks might not be a solution preferred by some (Marangoni, 2007), there are still unanswered questions regarding the use of surfactants derived from mixed, short or longer chain fatty acids (Vereecken *et al.*, 2009a; b). Pernetti *et al.* (2007) suggested that longer chains tended to have more structuring potential per gram of material than shorter chains. Further investigation of how these subtle variations in the amounts and chain length of structurants influence the structural properties of structured oil systems seems of interest, especially if combined with surfactants of different molecular structure, for example, monodiglyceride and polyglycerol polynicinate – a classical combination, for low fat water in oil emulsions. Indeed, explanation of these mechanisms is still required (Awad & Sato, 2002; Sakamoto *et al.*, 2003). Sakamoto *et al.* (2003) reported that polyglycerol behenic esters promoted nucleation, but inhibited crystal growth of palm oil and promoted the β' polymorph. Arima *et al.* (2007) reported that stabilisation and retardation effects allowed heterogeneous crystallisation (figure 4) and prohibition of morphological change, because of adsorption at the interfacial membrane. This is a mechanism proposed for templating nucleation (figure 5) and is interesting for low saturated fat systems, where an aqueous phase is included. It is possible that this approach could be useful for nucleation events within organogels, where Duffy *et al.* (2009) and Pernetti *et al.* (2007) suggest mixed systems that employ surfactants, and could offer advantages for structuring of oilcontinuous emulsions (and in specific cases water continuous emulsions), as many food products are emulsions.

It would be useful to know how alternative "host surfactants" might work with other surfactant combinations (Fujiwara *et al.*, 2000; Sakamoto *et al.*, 2003, 2004). The presence of interfaces, as in emulsions, will influence the creation of building blocks as required for oil structuring. Ishizuka *et al.* (2009) reported that surfactant molecules in water and other solvents can form various self-assembled structures such as micelles and liquid crystals, due to their hydrophobic interaction. The authors found micellar shapes could form varied spherical, to worm-like structures, depending on composition, temperature and other factors. These micelle formations grow to form aggregates and behave like polymers, becoming highly viscoelastic and can entangle each other (Duffy *et al.*, 2009). Therefore, translating these structuring options to emulsions will likely necessitate reformulation. This suggests that rather than focus purely on single components, or perhaps mixed bulk organogel systems, investigation into real systems where aqueous phases are employed could provide useful information (Pernetti *et al.*, 2007; Tanaka *et al.*, 2009).

In the case of a given interfacial emulsifier concentration, temperature, and shear rate, the surface of water droplets will be optimally or sub-optimally covered, especially in the context of HIPREs. Explaining these mechanisms could be problematic, in that laboratory scale techniques using standard methods could be limited because of their inability to provide data whilst under true dynamic conditions. During isothermal conditions, the mechanical orientation of TAG and non-TAG structures and stabilisation could be critical, especially where, for example, TAG structures in themselves do not exhibit polar behaviour. However, at a certain surfactant concentration, the TAG crystals become more polar in behaviour because the surfactant is adsorbed to the TAG surface which theoretically produces more rigid and uniform structures. Evidence suggests that at certain concentrations and ratios of specific surfactants (template additives), the surface of water droplets is more optimally covered because of faster induction of heterogeneous nucleation to

form molecular aggregates, which act as a template for nucleation.

Through use of SR- μ -SAXD microscopic analysis of the lamellar plane directions and structural domains could also be performed which might provide a deeper insight into the emulsion crystallisation mechanics.

Understanding how to measure mechanical viscoelastic properties of structurant interactions, both in model and real-time dynamic measurements, for example, UVP-PD, will be necessary (Pernetti *et al.*, 2007; Povey *et al.*, 2007; Schaink *et al.*, 2007; Young *et al.*, 2008; Arima *et al.*, 2009; Ishizuka *et al.*, 2009; Ojijo *et al.*, 2009; Rogers, 2009; Wassell *et al.*, 2010).

CONCLUSION

This review has looked at several systems considered able to structure low saturated fat-based systems and which in themselves could also have emulsification properties. The presence of interfaces, as in emulsions, will interact with the creation of building blocks as required for oil or fat structuring. Although many food products are essentially emulsions, interest in the structuring of oil-continuous emulsions (and in specific cases water-continuous emulsions) will not be straightforward, especially where some more novel structuring materials are used either wholly or partially to replace traditional structurants.

In attempting to reduce the degree of saturates in food systems, it will be necessary to observe effects on mixed structurants and to analyse this relationship when cosurfactant structures are used and how this may influence interfacial film thickness, strength and flexibility.

Understanding how to measure mechanical viscoelastic properties of structurant interactions both in model and real-time dynamic systems will be necessary to account for diffusion, orientation and self-assembly mechanisms. In the case of exploring how novel structures behave within W/O or O/W emulsions, it will be important to understand how interfacial active emulsifiers will behave at these surfaces to form heterogeneous structures.

Clearly, greater understanding of the role of these factors will require further investigation.

The authors consider that the answers to these problems are most likely to be achieved through three main routes; (1) combining traditional techniques with novel structurant technology; (2) developing and validating in-line dynamic measurement techniques; and (3) investigation of emulsion systems, as opposed exclusively to single phase model systems.

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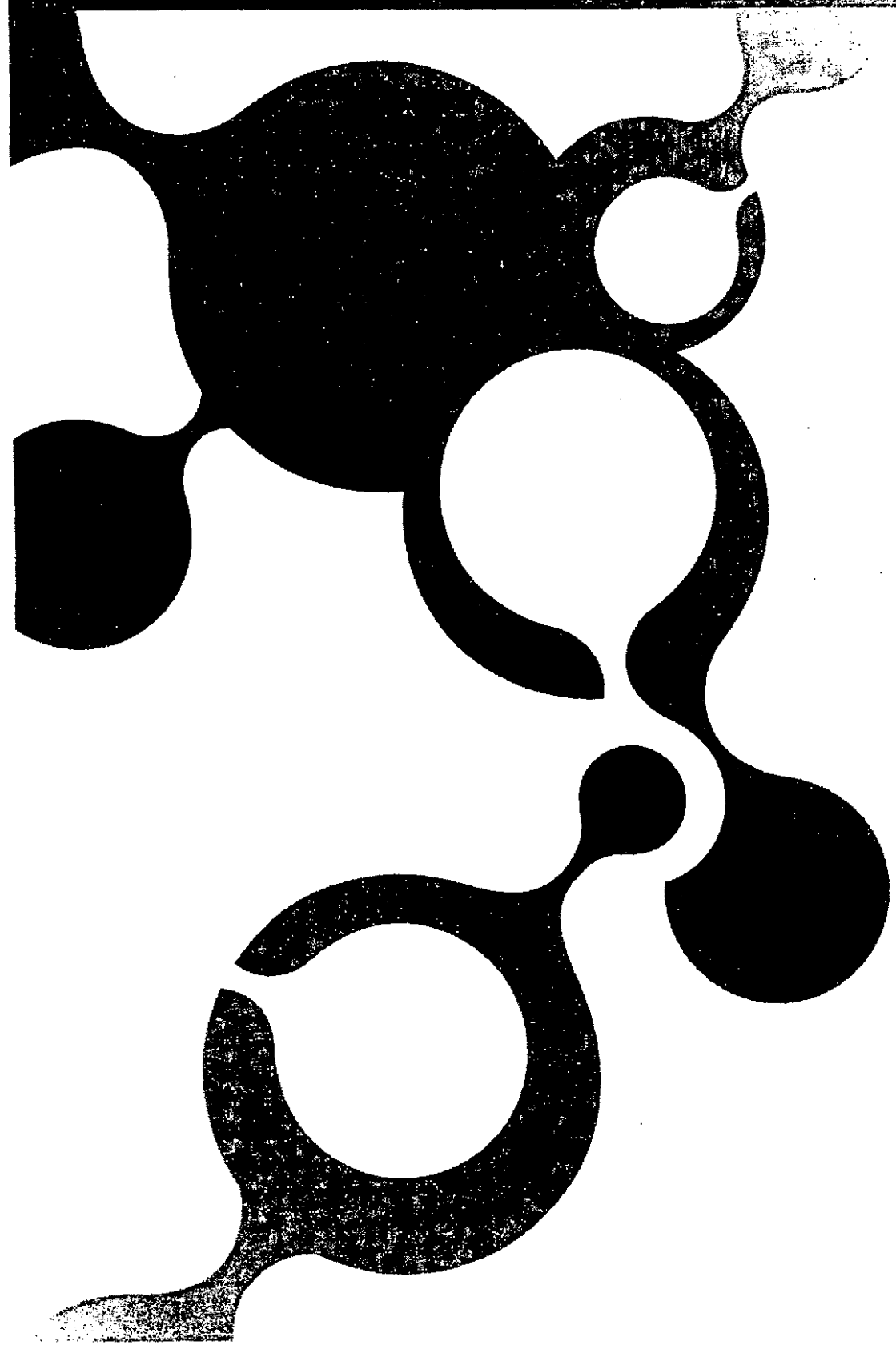
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Towards a multidisciplinary approach to structuring in reduced saturated fat-based systems – a review

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SUMMARY

Although many food products are essentially emulsions, interest in the structuring of oil-continuous emulsions (and in specific cases water-continuous emulsions) is intense, particularly to meet the continuing challenge of reducing the degree of saturates in food systems. Consequently, it is necessary to observe the effects of structurants and to examine their impacts on current food systems. This is especially the case where novel structuring materials are used to wholly or partially replace traditional structurants. A multidisciplinary approach is discussed encompassing traditional and novel mechanisms considered able to structure within low saturated fat-based systems and which in themselves could also have emulsification properties. The presence of interfacial compositions as in emulsions requires a crucial understanding of the interactions within these compositions for the creation of building blocks in oil or fat structuring. Where a co-surfactant structure may be used, together with novel structurants, for example, wax esters, phytosterols, it is necessary to understand how these may influence interfacial film thickness, strength and flexibility. Understanding how to measure mechanical visco-elastic properties of structurant interactions both in model and real time dynamic measurements will be necessary to account for diffusion, orientation and self-assembly mechanisms.

This review discusses combining traditional techniques with novel structurant technology; developing and validating dynamic measurement techniques; and investigation of real systems as opposed to purely model systems.

INTRODUCTION

The issue of *trans* fatty acids (TFA) replacement has been the subject of intense discussion and debate within the food industry as well as in the clinical field, with

a strong focus on reducing total saturated fatty acid content for health reasons (Berger, 2009; Fletcher, 2006; FSA, 2008). Achieving this is not simple, because many consumers expect particular textural properties in a given food product. The aroma, texture and mouth sensations experienced when consuming these foods are strongly dependent on their fat content and can eventually shape dietary choices in the long term (Drewnowski *et al.*, 1989; Drewnowski & Almiron-Roig, 2009). Thus, the idea of reformulating familiar foods which historically contained significant amounts of fats and oils (and usually contain significant levels of saturated fat) into lower fat versions is challenging not only technologically but also from a consumer acceptance point of view. Research into consumer perceptions of a new food product is often compared with memorised experience from a similar consumed food. Consumers may tend to conclude their decisions on the basis of their memory of a food, and not on the basis of their actual perceptions (Mojet & Koster, 2005; Morin-Audebrand, 2009).

It is reported that the consumption of TFAs may raise low-density lipoprotein (LDL) cholesterol levels, and lower high-density lipoprotein (HDL) cholesterol levels, thus contributing to atherosclerosis and an increased risk of apoplexy (European Food Safety Authority, 2004; FSAI, 2008; Gidding *et al.*, 2009). However, there is still debate as to the relevance of the intake of TFA from naturally occurring ruminant sources (Willett & Mozaffarian, 2008) and of the importance of saturated fats. McNeill (2009) clearly showed that despite a large body of epidemiological data being generated over the last two decades in respect of their adverse effects, there are also apparently certain important positive effects. Thus the effects of saturated fats on cardiovascular disease are complex.

Legislation, and literature (Dubinsky, 2008; Mozaffarian *et al.*, 2006; Stender & Dyreberg, 2003; Stender *et al.*, 2006; WHO, 2007) state that *trans* fatty acids should be removed from food, but current research (Stender *et al.*, 2009) suggests that this is insufficient in terms of creating healthy foods. Removal of, or at least drastic reduction of, not only *trans* containing fats, but all saturated fats is also required (Merchant *et al.*, 2008; SACN, 2007; Wassell & Young, 2007; Young & Wassell, 2008).

Realising the legislative requirements of governments, and consumer expectations for the food industry, is a tremendous challenge (Pernetti *et al.*, 2007). Achieving this balance of adequate structure in fat-based food systems whilst lowering the total saturated fatty acid content is a major objective of the food ingredient industry which remains elusive. For well over a decade the issue of *trans* fatty acid removal from bulk fat based systems has been the main focus of research in this field (Wassell & Young, 2007), and in some countries remains so (Benincá *et al.*, 2009; Willson, 2009), for example, Brazil and USA, respectively. However, the predominant global attention is in reducing total saturated fats, which of course includes *trans* fats (FSAI, 2008; L'Abbé *et al.*, 2009; Rogers, 2009; Wassell, 2010; Willett & Mozaffarian, 2008; Willson, 2009; Young & Wassell, 2008). However, whilst the problem is global, for some cases in emerging economies, the degree of importance placed on providing food products with lower *trans* and saturated fats has taken lower priority (Pérez-Ferrer *et al.*, 2010). Whilst there is general agreement that total fat levels should be reduced, there is disagreement as to the best route (Montague-Jones, 2009). Talbot *et al.* (2007) advocate the use of saturated fats preferably from natural sources. Others agree suggesting for example, that movement to reduce dairy food consumption

(and hence saturated fatty acids) irrespective of the nature of the dairy product should be made with caution (German *et al.*, 2009; SACN, 2007). Marangoni (2007) suggests that the use of saturated fat in the absence of *trans* fats is not a solution. As a result, alternative mechanisms for providing structure without saturated and/or *trans* fats to allow edible oil structuring have found increasing attention (Bot *et al.*, 2009b; Hughes *et al.*, 2009; Rogers, 2009).

Recent studies explore the different strategies including lipid crystal engineering (Schaink *et al.*, 2007); phytosterol systems (Bot *et al.*, 2009b); organogel-based emulsion systems (Duffy *et al.*, 2009) and wax technology to form "lipo-colloid" structures (Shigemitsu, 2006). A comprehensive discussion of current possibilities is proposed by Pernetti *et al.* (2007), who state succinctly that finding alternatives to traditional triacylglyceride (TAG) structuring whilst maintaining healthy properties, versatility and performance, is a tremendous challenge.

The aim of this review is to highlight the current state of the art, and propose a multidisciplinary-based approach to achieving the goal of providing structure for low saturated TAG systems and characterising these by means of new analytical approaches, which may include measurements within both static (Arima *et al.*, 2009; Tanaka *et al.*, 2009) and dynamic conditions (Wassell & Young, 2007; Young *et al.*, 2008; Wassell *et al.*, 2010).

TAG STRUCTURING

Traditionally, where TAG structuring is used, hard fractions and/or modified hard stocks composed largely of saturated fatty acids, also contained significant amounts of *trans* isomers (Kodali, 2005; Flöter & van Duijn, 2006; Podmore, 2008; Wassell, 2010).

Modification techniques and even the simple selection of alternative oils, for example, rice bran oil, shea, moringa, allanblackia (Lalas & Tsaknis, 2002; Most *et al.*, 2005; Garcia, 2006; Ghosh, 2007), have demonstrated the possibility of minimising and controlling the *trans*/saturated content

of oil blends and to successfully formulate alternative hardstocks (Abdulkarim *et al.*, 2005; ACNFP, 2006; Bell *et al.*, 2007; Annon, 2008; MacKenzie, 2008; Lerma-García *et al.*, 2009; Mayamol *et al.*, 2009).

The combination of techniques leads to a greater variety of hardstocks with a wider range of physical properties such as solid fat content and melting profile. This is particularly important for fats from which a specific performance is expected. Exclusive focus on the physico-chemical aspects but neglecting the fat's required functional role within the final application leads to other problems. Matching the physical properties of a commercial fat blend to a specific application is normally based on solid fat profile, melting point and textural qualities. Subsequently, the commercial fat blend's plastic range might be expected to be within a given tolerance (Young & Wassell, 2007; Wassell, 2010). Ultimately, the reason for this is to fulfil performance phenomena such as creaming, crystallisation and emulsification, which also need to be considered. Therefore, fatty acid composition, polymorphism and process conditions can not be ignored. Concentrating exclusively on the fat phase does not necessarily address the whole challenge in the case of reducing total saturates, for example, addition of a water phase, creating an emulsion, which automatically reduces the fat content in the final application. However, to effectively pursue this strategy often requires balanced emulsifier technology and possibly the use of other additives, and even subsequent redesign of the final food product may be necessary (Wassell & Young, 2007). It is known that the composition, polymorphism, solid fat content and microstructure of TAGs all play a crucial role in the structure of lipid-based products (Christie, 1982; Timms, 1985; Garti & Sato, 1988; Larsson, 1994; Narine & Marangoni, 1999; Hartel, 2001; Rogers, 2009). The major advantage of TAG structuring is the diversity of the molecules and molecular configurations, which allows for the physical properties to be tailored to the final application by changing the chemistry of the molecules or by modifying the processing conditions,

enabling production of solid and semi-solid fats (Bailey's, 2005; O'Brien, 2009).

HYDROGENATION

Hydrogenation or partial hydrogenation processes, which have been commonly used in the modification of oils for food product formulations, are able to deliver specific, desired melting behaviours for fat blends (Hamm & Hamilton, 2000; Gunstone, 2002; Podmore, 2008; Dijkstra, 2009). The proportion of fatty acids which can be changed through hydrogenation is classified as unsaturated fatty acids, having one (monounsaturated), two or three (polyunsaturated) double bonds. These types of fatty acids usually have the *cis* configuration, that is, the hydrogen atoms with respect to the double bond are on the same side of the molecule. Fully saturated fatty acids do not contain double bonds and are least reactive chemically (O'Brien, 2009).

Addition of hydrogen atoms across the unsaturated double bonds, causing saturation of the TAGs, causes more rigid structures because of the new molecular configurations. Apart from removing or shifting the double bond, the same process can also cause the *trans* configuration associated with negative health effects (Stender & Dyreberg, 2003). Fatty acids specified as being in the *trans* configuration have the hydrogen atoms on the opposite sides of the molecule, and the molecule assumes a nearly linear configuration similar to saturated fatty acids. Hence *trans* fats behave more like saturated fatty acids. Partial hydrogenation, which is carried out to alter the plasticity and functional properties of a fat, produces several *cis* and *trans* fatty acids from intramolecular rearrangements. Irrespectively, any increase in saturation results in higher melting point of the TAG, and therefore, is more solid at room temperature (Foster *et al.*, 2009). Importantly, as mentioned during the introduction, not all *trans* fatty acids are produced by commercial hydrogenation (SACN, 2007; German *et al.*, 2009). Indeed there is intense debate where dairy fats are concerned and a need to differentiate between effects of hydrogenated and naturally occurring *trans* fats (Kummerow,

2009). Options to reduce the *trans* levels during the hydrogenation process of edible oil have been investigated (Beers, 2007).

INTERESTERIFICATION

In view of the limited ability of solidifying "natural" TAGs to create certain structures, other naturally occurring hardstock components, that is, from palm oil are used. The basic principles of interesterification were first documented by Fondu & Willems (1969) and they described a process which resulted in the rearrangement of the distribution of the fatty acids either chemically or enzymatically, within and between the triglycerides. Consequently, the fatty acid distribution is altered but the fatty acid composition remains unchanged – this rearrangement can occur either in a random or controlled manner (Yusoff & Dian, 1995). The net effect of rearrangement leads to production of oils that require a certain semi-solid-plastic range having different levels of structure, each influencing the macroscopic properties of the material (Tang & Marangoni, 2006a; Ribeiro *et al.*, 2009).

FRACTIONATION

The controlled crystallisation of TAGs can result in the separation (fractionation) of a solid phase (stearin) and a liquid phase (olein). In turn, these can be further fractionated (van Duijn *et al.*, 2006).

Essentially, the process of fractionation consists of crystallisation to produce solid crystals in a liquid matrix, and separation of the crystals from the liquid matrix (Timms, 1997). Fundamentally, fractionation processes work to the following principles: complete melting of the fat, slow cooling, gentle or no agitation to encourage the development of large crystals and separation into liquid and solid fractions with differing physical and chemical compositions (Timms, 2005). An excellent review by Timms (2005) discusses the different fractionation methods, and Dijkstra (2009) provides information on recent developments not just in fractionation, but reviews edible oil processing generally.

Palm is probably the most important oil in terms of fractionation because of its

unique fat profile (Sahasranamam, 2005) which can be broken down into individual fractions (Timms, 2007). Another term used for fractionation is winterisation, and is essentially the process of removing wax esters and high melting TAGs at lower ambient temperatures, and still has modern use today particularly for oils liquid in the ambient temperature range (MacKenzie, 2008).

Fractionation has been shown to be useful in the replacement of some emulsifiers – specifically highly saturated emulsifiers, with low iodine values, which are difficult to replace with non-hydrogenated emulsifiers. To supply emulsifiers, which have the same physical/chemical characteristics as the widely used hydrogenated types, but preferably, in a non-hydrogenated form is challenging.

It is the more saturated, and preferably the fully saturated monoglycerides which are able to assist in both emulsification and promote crystallisation. An example is in the preparation of emulsions for industrial margarines, which typically require use of simple monodiglycerides. Bech *et al.* (2008) describe a method of preparing a non-hydrogenated emulsifier having substantially no *trans* carbon-carbon double bonds, and further discusses other surfactants which are built on "natural"

feed stocks, which may be fractionated, to give remarkably low iodine values; an indicator of the degree of saturation.

Talbot *et al.* (2007) favour fractionation for design and control of the fat blend due to it containing a significant portion of high melting TAG's (Lida & Ali, 1998; Sundram, 2005). Timms (2005) neatly summarises the whole mechanism and comments that with the decline in hydrogenation, interesterification has seen a renaissance, although it is only partially able to replace hydrogenation. Additionally, interesterification suffers from the "chemical"-process image and environmental drawbacks of hydrogenation. Therefore, fractionation, a purely physical process, more adequately satisfies today's increasing environmental and health concerns.

NON-TRADITIONAL STRUCTURANTS

As TAGs are responsible for the network structure in traditional systems, it is difficult to entirely remove saturated fats without compromising some sensory and physical characteristics. Alternative structurants for discussion are listed in figure 1. Several reviewers acknowledge the necessity to revisit some of the traditional solutions and couple these with the use of novel materials, because it is unlikely that one novel structurant, for example, mixture

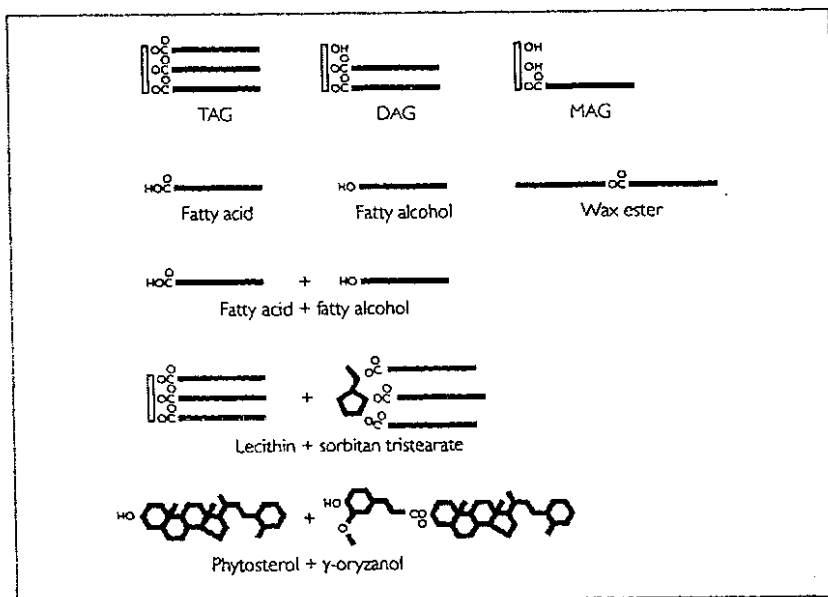


Figure 1. Schematic representation of a number of structurants for TAG oil phases (Pernetti *et al.*, 2007).

of phytosterols and oryzanol could satisfy all requirements. Rather, this mixture in a TAG-based, water-in-oil emulsion with a surfactant is more realistic (Pernetti *et al.*, 2007; Schaink *et al.*, 2007; Bot *et al.*, 2009b). Therefore, textural properties to which consumers are accustomed may not be achieved through singular techniques. It is likely that synergies obtained through combining disciplines, understanding of thermodynamic mechanical properties and critical design of real systems, will play a vital influence (Fornuso & Akoh, 2001; Pernetti *et al.*, 2007; Duffy *et al.*, 2009; Hughes *et al.*, 2009; Rogers, 2009). Therefore, it is suggested that a multidisciplinary approach to the study, design and possible solution of the problem is necessary (Wassell & Young, 2007; Young *et al.*, 2008; Wassell, 2010).

TAG

Apart from that discussed in the TAG structuring section, Higaki *et al.* (2003) observed gel-like behaviour in TAG mixtures of fully hydrogenated rapeseed oil with behenic acid concentrations of 1.5–4.0 wt%. Rapid cooling and heating to final temperature were necessary to achieve gel-like behaviour, whereas simple cooling without a cooling/heating procedure did not form a gel-like fat mixture. This is attributed to cooling rate, agitation and degree of supercooling, control the rate of crystal growth and thus crystal size and crystal agglomeration, which affect the textural and melting properties of the fat product (Humphrey & Narine, 2004). Importantly, Higaki *et al.* (2003) was able to influence polymorphism by adjusting thermal treatment and tempering, to achieve a β -gel without waxes, or other emulsifier additives. The subject of polymorphism is not discussed in any detail within this review, and good explanations are provided within the literature (Hernqvist, 1984; Sato, 2001).

Mentioned in the previous section, Pernetti *et al.* (2007) discusses several mixed structurant systems could benefit from utilising TAGs with novel structurants under specific process conditions, a multidisciplinary approach. This will subsequently be enlarged upon during this discussion

(Wassell & Young, 2007; Young *et al.*, 2008; Hughes *et al.*, 2009; Wassell, 2010).

DAG

Pernetti *et al.* (2007) note that surprisingly little attention has been given to structuring using diacylglyceride (DAG or diglyceride), and the authors cite dipalmitin and distearin as forming crystalline networks in a similar way to those formed by TAGs. These gel formations are slightly softer than TAG crystal networks of similar concentration. Indirectly, the reduction and influence of diglyceride content can also play a positive effect as a β -stabiliser (Hernqvist & Anjou, 1983; Cheong *et al.*, 2009), which has not really been exploited (Kristensen *et al.*, 2005). The reduction of diglycerides in palm oil rich blends, can lead to an increase in the total solid fat content. Thus, it is possible to produce similar viscoelastic profiles in products, normally associated with a higher degree of saturated fatty acids. Examples are: margarine, salad dressing products, nutritional bars, muffins, brownies, breads, cookies, doughs and batters for baked goods (Boice *et al.*, 2003; Sikorski, 2005; Kristensen & Wassell, 2006).

MAG

Monoacylglycerol (MAG or monoglyceride) components are able to structure both lipid and aqueous phases (Marangoni, 2007; Rogers, 2009; Rush *et al.*, 2009). MAGs are thought to form reversed bilayers in TAG oils. Ojijo *et al.* (2004a,b) investigated the formation of stable network structures through the cooling of mixtures of various concentrations of monoglycerides and vegetable oils. Mechanical hardness of olive oil/MAG gel networks was investigated. A given minimum monoglyceride volume fraction was necessary for formation of a gelled network. The onset of the gel network or structure formation was indicated by a change in the value of the elastic modulus, whilst network hardness increased with increase in MAG content. High cooling rates led to low final elastic modulus values but harder networks, whereas slow cooling rates gave the reverse. Maximum gel network development occurred with moderate shear rates, thereby highlighting

the fact that the physical and functional characteristics of such products, in this case, depend on processing conditions, cooling rate, shear and presence of co-surfactants (Ojijo *et al.*, 2004b; Pernetti *et al.*, 2007; Davis *et al.*, 2009; Hughes *et al.*, 2009; Krabbenhoft *et al.*, 2009; Rogers, 2009; Tippetts & Martini, 2009).

Novel structurants

Hughes *et al.* (2009) report that a number of organogelator systems have the ability to gel edible oils at very low concentrations (~0.5–2.0 wt%), and apart from those previously mentioned, include network-forming edible oil structurants: TAGs, DAGs, MAGs. Murdan *et al.* (1999) discuss sorbitan mono-stearate and Gandolfo *et al.* (2004) and Schaink *et al.* (2007) discuss mixtures of fatty acids and fatty alcohols. Combinations of lecithin and sorbitan tri-stearate, phytosterols and oryzanol have also been reviewed (Pernetti *et al.*, 2007). Other organogelators or mixtures are well-known for their ability to structure in edible oils: 12-hydroxystearic acid (Rogers *et al.*, 2007, 2008a,b, 2009), ricinelaic acid (Wright & Marangoni, 2006), candelilla wax (Toro-Vazquez *et al.*, 2007), mixtures of β -sitosterol and γ -oryzanol (Bot & Agterof, 2006). Rogers *et al.* (2009) also show that sphingolipids, like triacylglycerides, can exhibit variability in the fatty acid chain length. These are able to form long thin fibre structures, creating greater surface area and thereby stabilising more polyunsaturated liquid oil (Christie, 2010).

Irrespective of the network composition, organogels have numerous potential different functionalities in food products (Duffy *et al.*, 2009), and are not limited to oil mobility and migration, the replacement of saturated and *trans* fats, and the stabilisation of emulsions (Pernetti *et al.*, 2007; Rogers, 2009). Network forming modified polymers are known to have dual affect as structurant and surfactant capability at oil water interfaces, but these are usually non-edible applications, and therefore not within the scope of this review.

Other food grade polymers include cellulose derivatives including chitosan (Pszczola, 2006; Rietberg & Marangoni,

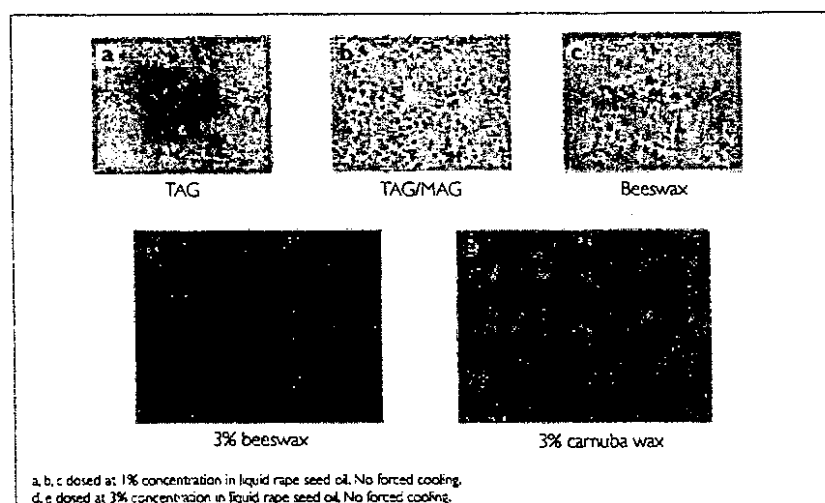


Figure 2. Waxes compared with traditional TAG and monoglyceride (MAG) (M. Nielsen, unpublished data).

2009), however, the use of these materials for edible oil structuring is rare due to restrictions on modifications for food use (Pernetti *et al.*, 2007) and therefore applications tend to be associated to oil-in-water applications because cellulose derivatives such as cyclodextrins must be fully hydrated for functionality (Cui & Wang, 2006).

Waxes/fatty acids/phytosterols

Experimental application of wax in peanut butter provides an example of a multidisciplinary approach, where a naturally slow crystallising beeswax is used to replace traditional TAG based hardstock. A "lipocolloid" – like network is formed, with efficient needle shaped structures, rather than spherical shaped particles (Pernetti *et al.*, 2007). Waxes compared with traditional TAG and MAG solutions are shown in figure 2. In liquid oil, similar yield stress values can be achieved using lower inclusions than typical TAG or MAG concentrations (M. Nielsen, unpublished data). Mellema (2009) studied co-crystallisation of beeswax and various vegetable waxes with sterols and reported that rice bran wax, sunflower wax and jojoba can increase crystal events in a formulation. Furthermore, Mellema (2009) highlighted the benefits of heRP70 (fatty acid composition: C16:0–5%, C18:0–40%, C20:0–9%, C22:0–43% with more than 99.5% total saturated fats), reporting the replacement of beeswax with combina-

tions of heRP70, sunflower oil, or jojoba wax also significantly increased the amount of crystalline material in the formulation. This was attributed to improved solubility of the sterols. This provides scope for combining traditional and novel solutions (Pernetti *et al.*, 2007). Toro-Vazquez *et al.* (2007) established the oil structuring property of candelilla wax in safflower oil at concentrations of ~1 wt% and higher. Kodali (2009) also reports Ricebran wax being able to stabilise other long chain polyunsaturated oils.

Dassanayake *et al.* (2009) report network formation of rice bran wax crystals and show organogel properties occurred more rapidly, coinciding with temperatures of crystallisation than that of the mixtures of carnauba wax and candelilla wax in olive oil. The same authors also observed a low concentration of carnauba and candelilla wax was necessary to form an organogel in olive oil at 4 and 2 wt%, respectively. Gel structures formed soon after rice bran wax crystallised, whereas a time delay was observed between the organogel formation and wax crystallisation of carnauba wax and candelilla wax, demonstrating rice bran wax has good organogelforming properties. The quicker gelation in the rice bran wax system was attributed to comparatively longer fibrous crystals of rice bran wax which form gelator networks efficiently entraining the liquid oil.

Martini *et al.* (2008) discuss two different crystal populations when testing sunflower oil wax (SFOw) in anhydrous milk fats (AMF) and suggest the presence of two different populations of crystals. This could be attributed to differences in the molecular weights of SFOw and AMF, where the AMF at high temperatures crystallise very slowly forming large agglomerates. These authors found that the addition of SFOw could decrease the induction time of crystallisation, promoting crystallisation, especially towards high temperatures. Dassanayake *et al.* (2009) reported the presence of different components within the wax, which seemed to have a profound effect on the crystal habit of the plant wax–vegetable oil organogels. Conditions of organogel preparation (e.g. degree of agitation, cooling rates and storage conditions) were likely to influence crystal morphology of the gelators.

Mellema (2009) investigated methods for solubilising sterols, which in themselves form structures, but can be difficult to incorporate into TAG systems (Pernetti *et al.*, 2007; Hughes *et al.*, 2009; Rogers, 2009). Mellema (2009) found that mixing molecularly similar waxes, including ursolic acid (found within apple waste) facilitated the incorporation of sterols. Bhagga *et al.* (2002) showed that by adding a blend of ursolic acid and oleanolic acid to a fat per se or to a fat in a food product, the crystallisation rate of the fat could be increased concomitantly with the hardness of the fat composition. Furthermore, it was found that the addition of the ursolic acid/oleanolic acid mixture also improved other properties of the total composition, such as oral mouthfeel, heat resistance, and aeration properties. Combining waxes and specific fatty acids, might be suitable, because of their similar hydrophobicity to sterols and their typical plasticity, which allows a structural "flexibility" for the sterols to fit into a crystal network (Mellema, 2009).

Organogel – phytosterol emulsions/ 12-hydroxystearic acid

Little is known about the structures formed in specific organogels and how these structures might behave at the emul-

sion interface. Duffy *et al.* (2009) studied oil-in-water organogels based on edible oils and specific mixtures of phytosterols, in an attempt to describe and understand micro-structural features, prepared using basic processing conditions. They showed that long thin crystals are formed extending out of the oil phase into the continuous water phase. These emulsions of phytosterol-based organogels in an aqueous solution formed with the presence of emulsifiers and resulted in the formation of small emulsion droplets; internal oil droplet structure was not studied. Schaink *et al.* (2007) showed that lipid crystal engineering using mixed crystals offers the prospect of obtaining harder organogels with less structurant. A possible application of this type of structurant mixture is the replacement of saturated fats in a broad range of water-in-oil products. For these applications, it is important to know whether the mixed crystals also contribute to the visco-elastic properties of W/O and O/W emulsions that are made using these structurants. Observing and explaining these effects is of technical relevance and should be investigated. Schaink *et al.* (2007) suggested that it would be interesting to combine different approaches in order to obtain an insight into the mechanism of organogel formation, which may lead to improved understanding of the polymorphism and crystal formations resulting from mixed components. Ishizuka *et al.* (2009) reported that surfactant

molecules in water and other solvents can form various self-assembled structures such as micelles and liquid crystals, because of their hydrophobic interaction. The micellar shapes can vary from spherical to worm-like structures, depending on composition, temperature and other factors. When micelles grow to form aggregates and behave like polymers, becoming highly visco-elastic, they may entangle each other.

"Self-assembled fibre networks" (SAFiN) are well reported (Pernetti *et al.*, 2007; Rogers *et al.*, 2008a; Rogers, 2009) and spontaneously form fibres, capable of structuring the oil phase. Duffy *et al.* (2009) report systems able to form structure in the aqueous phase, and it has been confirmed (Bot & Agterof, 2006; Bot *et al.*, 2008; 2009a) that β -sitosterol – γ -oryzanol fibril systems are quite unique as they are one of the few combinations capable of forming fibril structures in both aqueous and oil systems. Both Duffy *et al.* (2009) and Ishizuka *et al.* (2009) report formation of micellar tube-like structures (figure 3) in the aqueous phase. They found their formation to be time and temperature dependent and they concluded that a diffusion-based mechanism might occur, in which the sterols or sterol containing features move and rearrange from the lipid phase into the aqueous phase. Duffy *et al.* (2009) show that sterol solubility in edible oil is further reduced with the transition from a pure organogel system

to an organogel-based emulsion system, and explained that in hot dry vegetable oils sterols are reasonably soluble, but this decreases in oil saturated with water (Jandacek *et al.*, 1977; Duffy *et al.*, 2009). This has implications, because depending on the presence of another co-structuring material, for example, lipid; it may affect diffusion, and integration kinetics differently (Povey *et al.*, 2007).

The above observations have significance not only to the understanding of how these structurants are behaving in model systems but also to their behaviour in "real" emulsions. This raises the question of how combinations of such structurants may perform both thermodynamically and mechanically at the interfaces of O/W or W/O emulsions (Bot *et al.*, 2009a,b). Thus the question of phytosterol solubility and its potential structuring ability requires further investigation. Understanding how to measure mechanical visco-elastic properties of structurant interactions both in model and real time dynamic measurements (Povey *et al.*, 2007; Ishizuka *et al.*, 2009; Ojijo *et al.*, 2009) will therefore become increasingly necessary (Pernetti *et al.*, 2007; Schaink *et al.*, 2007; Arima *et al.*, 2009; Rogers, 2009; Tanaka *et al.*, 2009; Young *et al.*, 2008).

Application of alpha (α) polymorphic tending emulsifiers (Stauffer, 1999) in liquid vegetable oil to form a soft gel mixed into the aqueous phase has been reported (Wassell, 2006a,b). The α crystalline form is more flexible than the rigid beta (β) crystalline form and rearranges more easily during heating cycles. The former establish a physical film at the interface of the oil droplets and prevent inhibition of foam formation with relatively low levels of total oil/solid fat. This provides a significant reduction of total saturates (Wassell & Young, 2007). A suppression of the solid fat content is also observed with additions of between 5 and 10 wt% mixed, fully hydrogenated surfactants (Wassell, 2006a,b). Suppression, and time delay of solid fat content is also reported by Hughes *et al.* (2009) where addition of 2% w/w 12-hydroxystearic acid (12-HSA) to a model filling (60:40 canola

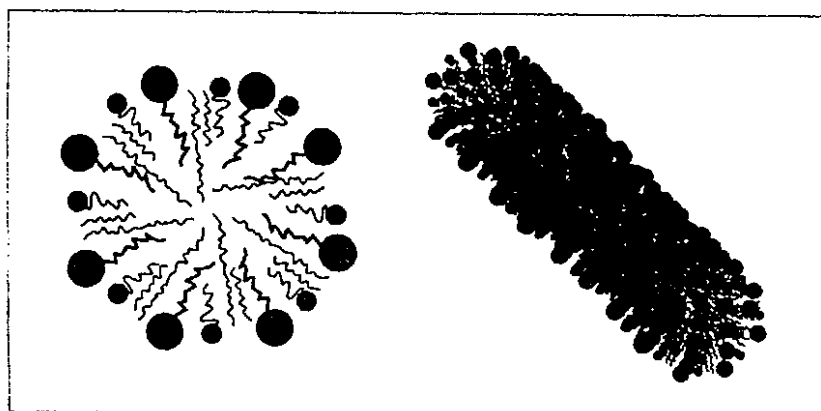


Figure 3. Schematic diagram (hypothetic model) of the ordering of the two sterol species with triacylglycerides in a 10-nm tube structure. The molecules are drawn on scale approximately. Red γ -oryzanol, green β -sitosterol; "chair-model"; triacylglycerides. The right image shows a schematic diagram of the tube structure; organisation of the sterols with respect to each other may be more random. Adapted from Duffy *et al.* (2009).

oil:interesterified hydrogenated palm oil) composite cream-filled confection, did not increase the solid fat content of the mixture. Isothermal crystallisation occurred at 20 °C. The authors explained that 12-HSA is a high melting point lipid component, and therefore, theoretically the SFC of the mixture would be expected to increase proportionally with its addition. However, its inclusion did not translate to a higher SFC and therefore addition of 12-HSA either delays or slows normal crystallisation (Hughes *et al.*, 2009).

Hughes *et al.* (2009) proposes potential food applications of edible oil organogels and emulsions, reporting the complexity of network formation and bonding interactions, and is considered difficult to design systems or predict which organogelators will work with a particular solvent, therefore immobilised water droplets within a continuous gelled oil phase were investigated. Hughes *et al.* (2009) suggest that given certain formulation and processing conditions, organogelled emulsions may have application as low-fat spreads or to control the release of both hydrophilic and hydrophobic bioactive (probiotic) compounds (Hughes *et al.*, 2009).

Hughes *et al.* (2009) report the potential application of water-in-gelled-oil emulsions, where addition of typical food grade emulsifiers (i.e. Span 60 or Tween 80) drastically modified the textural properties which can negatively affect the ability of 12-HSA to gel oil. 12-HSA is not considered a food grade additive as it is derived from castor oil and is considered an irritant, although Rogers (2009) reports it as being an ideal compound for examining macroscopic changes in processing conditions. Others have recently investigated and studied the physico-chemical, self-assembling behaviour and potential of 12-HSA, to form tube like structures. Additions in excess of 30% of other lipids (saturated fatty acids), or phospholipids could be incorporated without negatively affecting structure (Fameau *et al.*, 2010).

Crystal habit modifiers and co-gelators

Recent publications have discussed the use of "crystal structure modifiers" (Garbolino

et al., 2005; Rousseau *et al.*, 2005; Permetti *et al.*, 2007; Young *et al.*, 2008), addition of a co-surfactant (Foster *et al.*, 2007; Rogers, 2009), inclusion of an additive, accelerant (Katsuragi, 1999; Fujiwara *et al.*, 2000; Wassell *et al.*, 2010), or impurity (Awad & Sato, 2001, 2002).

Crystal structure modifiers are potentially interesting not only within traditional systems, but also within novel structures and mixtures (Permetti *et al.*, 2007). Effects of, hydrophobic, adsorption properties of additives and template behaviour for acceleration of surface heterogeneous nucleation events have been studied (Awad & Sato, 2001, 2002; Cerdeira *et al.*, 2003, 2005, 2006; Sakamoto *et al.*, 2003, 2004). More recently, the behaviour of unsaturated and saturated surfactants, their polymorphism, time temperature effects and advanced analysis (Arima *et al.*, 2009; Tanaka *et al.*, 2009) has provided information on the interactions of minor components (Vereecken *et al.*, 2009a) and crystallisation with and without water phase (Vereecken *et al.*, 2009b). Whilst all these observations are vital in providing understanding, it is also considered important to observe effects of mixed surfactant systems, and how these interactions influence their relative relationship in TAG and non-TAG mixtures (Permetti *et al.*, 2007; Rogers, 2009). Investigation of the kinetic stabilisation of emulsions with low concentrations of continuous phase crystals (Rousseau *et al.*, 2005) found polymorphic form and morphology could be manipulated through a multidisciplinary approach, involving dilution, tempering regime and the presence of polyglycerol polyricinoleate (PGPR), under different crystallisation conditions – this being static vs. dynamic crystallisation (Young *et al.*, 2008; Wassell *et al.*, 2010). Rousseau *et al.* (2005) suggest liquid emulsifiers such as PGPR compared with surfactants such as saturated MAG are not as likely to influence crystal lattices, unless PGPR is combined with agitation conditions, where polymorphic transformation was retarded. However, static crystallisation in the presence of PGPR showed no differences. This aspect could be especially interesting to observe in the area of high internal-phase-

ratio emulsions (HIPREs) (Charteris, 2007) where interfacial film strength and mechanical flexibility will probably impact on final structures resultant from adsorption, diffusion and integration kinetics (Povey *et al.*, 2007).

Attempting to modify structures based on traditional, novel or a combination of these approaches, and especially where thermodynamic conditions are combined with co-gelators such as mixed surfactants, could lead to some potentially interesting physical properties (Hughes *et al.*, 2009; Rogers, 2009). Recently Bot *et al.* (2009b) investigated the importance of the composition of emulsions based on β -sitosterol and γ -oryzanol and found that increases in phytosterols led to an increase in firmness of the emulsion gel and that changing the ratio of β -sitosterol to γ -oryzanol proved more sensitive than previously observed for the pure organogels (Bot & Agterof, 2006). Bot *et al.* (2009b) also found it more critical to use a 40:60 β -sitosterol to γ -oryzanol weight ratio in order to achieve the optimal emulsion firmness. The effects of a number of minor ingredients, including MAGs, and make up of the water phase, were also investigated. The authors concluded that water activity is not important for the emulsion's properties, and found the addition of MAGs reduced droplet size and improved spreadability (Ritter *et al.*, 2005). Bot *et al.* (2009b) speculated that smaller droplets cause smaller "defects" in the organogel network, leading to firmer emulsion gels, but seem to be sensitive to the combination of cooling and shearing normally used in W/O emulsion processes. Hughes *et al.* (2009) found similar challenges when investigating organogel emulsions based on 12-HSA, though ultimately finding 12-HSA crystals to be dispersed evenly throughout the continuous oil phase and were not present inside or concentrated at the surface of the water droplets. Fairly large water droplets were formed, but these were stable (Hughes *et al.*, 2009). Both examples from Bot *et al.* (2009b) and Hughes *et al.* (2009) highlight room for further improvement in the emulsion preparation process. Research from studies within other disciplines (Peng *et al.*, 2009) may provide clues to the

formation of HIPREs using cholesterol derivatives as natural emulsifiers. HIPREs emulsions contain an internal phase volume of 70% (v/v) or greater, forming dispersed polyhedral structures, separated by thin films of continuous phase. These highly concentrated emulsions are also called "gel-emulsions" because of their visco-elastic behaviour (Peng *et al.*, 2009).

TECHNIQUES FOR INVESTIGATION

Most studies have been performed under isothermal conditions where observation of crystal behaviour is potentially quite different from that observed within a dynamic environment (Garbolino *et al.*, 2005; Janssen & MacGibbon, 2007; Maleky *et al.*, 2007; Povey *et al.*, 2007; Wassell *et al.*, 2010). Interactions of and between surfactants and their interactions as template structures, for example, in heterogeneous nucleation events (Fujiwara *et al.*, 2000), are not easily explained with typical measurements such as rate of crystallisation tests – static conditions – zero shear, and synchrotron (X-ray/DSC) tests – static conditions – zero shear (De Graef *et al.*, 2006; Perneti *et al.*, 2007; Povey *et al.*, 2007). Improved understanding may therefore require the use of new techniques capable of observing and quantifying structural events in both static and under dynamic conditions (van Duynhoven *et al.*, 2005; Tang & Marangoni, 2006b; Arima *et al.*, 2009; Boodhoo *et al.*, 2009) and describing this relationship to their me-

chanical properties, for example, ultrasonic velocity profiling with pressure difference (UVP-PD) equipment allowing non-invasive in-line rheological measurement and synchrotron radiation microbeam small-angle XRD (SR- μ -SAXD) technique to more precisely observe microstructures of fat crystals (Prakash & Ramana, 2003; Mazzanti *et al.*, 2005; De Graef *et al.*, 2006; Maleky *et al.*, 2007; Perneti *et al.*, 2007; Young *et al.*, 2008; Tanaka *et al.*, 2009; Wassell *et al.*, 2010). Determination and validation of methods will of course have to be approached with caution, in order to obtain an understanding of the potential diffusion or self organising mechanical properties leading to achievement of clear rheological behaviours (Morales-Rueda *et al.*, 2009). Nucleation events, which are likely to be heavily influenced by small quantities of high melting fats, acting as seed crystals, may be difficult to establish with current analytical techniques. The surface integration of molecules into growing crystals can similarly be upset by small quantities of impurities. Further, where fat crystallisation occurs within emulsions, this introduces additional complications (Himawan *et al.*, 2006).

DISCUSSION

Two themes seem to run through the literature; first, the necessity to move away from the addition of hard fatty material and substitute by alternative structure forming strategies. Second (related to first theme) is the need to

cause accelerated nucleation events through inclusion of a small amount of additive such as a surfactant. Such technology is well documented (Sakamoto *et al.*, 2003, 2004) and commercialised (Neddersen *et al.*, 2009). Therefore, given the aforementioned approaches, there are two areas for consideration; not just structure and assembly within the bulk oil, but the mechanism of structure at interfaces, for example, water-in-oil emulsions, and how the interface might be modified through surfactant-initiated surface heterogeneous nucleation to provide adequate structure, strength, and flexibility through a range of mechanisms (Povey *et al.*, 2007).

It is probable that there is a mechanism which could employ the use of "traditional" TAG-based structurants, coupled with novel structuring types (Perneti *et al.*, 2007; Duffy *et al.*, 2009). For example, one of a range of previously discussed assemblies might be more efficiently optimised over shorter induction times, as a result of the inclusion of a material acting as an accelerant which might otherwise have been considered an impurity (Wassell *et al.*, 2010).

Structurants such as γ -oryzanol which work very well in bulk oil, may have limits within water-in-oil emulsions for products such as spreads, as they cannot provide the textural properties consumers are familiar with. However, modification of the thermodynamic driving force and addition

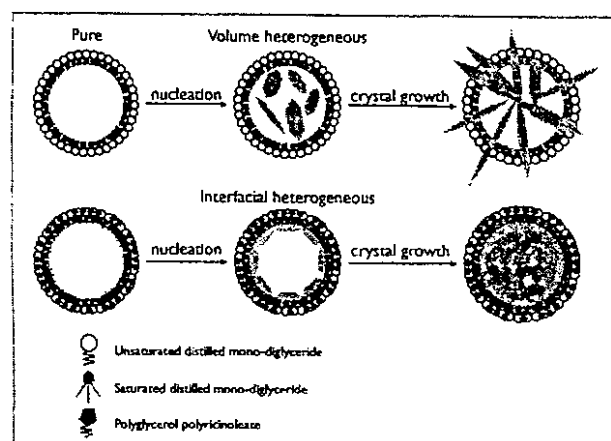


Figure 4. Heterogeneous crystallisation of O/W emulsion with additive. Adapted from Arima *et al.* (2007).

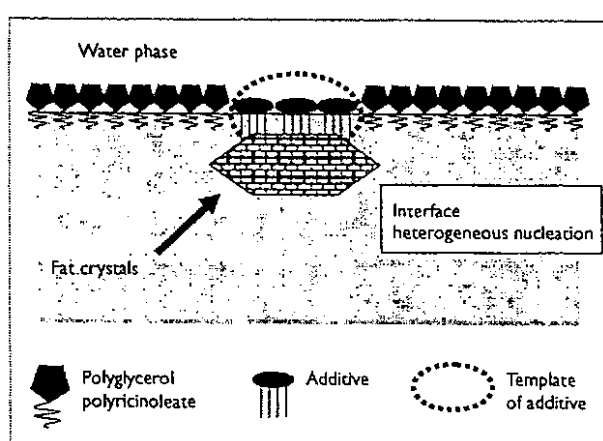


Figure 5. Additive to induce crystal nucleation, whilst retarding crystal growth. Adapted from Sato (2005).

of a co-surfactant (Foster *et al.*, 2007; Permetti *et al.*, 2007; Rogers, 2009) could achieve nucleation through standard accelerated induction events with inclusion of a surfactant, for example, monoglyceride.

Among the components discussed by Rogers (2009), fatty acids, particularly long chain fatty acids, are ignored due to the negative health implications associated with traditional fat based networks. However, whilst the use of saturated TAG networks might not be a solution preferred by some (Marangoni, 2007), there are still unanswered questions regarding the use of surfactants derived from mixed, short or longer chain fatty acids (Vereecken *et al.*, 2009a; b). Permetti *et al.* (2007) suggested that longer chains tended to have more structuring potential per gram of material than shorter chains. Further investigation of how these subtle variations in the amounts and chain length of structurant influence the structural properties of structured oil systems seems of interest, especially if combined with surfactants of different molecular structure, for example, monodiglyceride and polyglycerol polyricinoleate – a classical combination, for low fat water in oil emulsions. Indeed, explanation of these mechanisms is still required (Awad & Sato, 2002; Sakamoto *et al.*, 2003). Sakamoto *et al.* (2003) reported that polyglycerol behenic esters promoted nucleation, but inhibited crystal growth of palm oil and promoted the β' polymorph. Arima *et al.* (2007) reported that stabilisation and retardation effects allowed heterogeneous crystallisation (figure 4) and prohibition of morphological change, because of adsorption at the interfacial membrane. This is a mechanism proposed for templating nucleation (figure 5) and is interesting for low saturated fat systems, where an aqueous phase is included. It is possible that this approach could be useful for nucleation events within organogels, where Duffy *et al.* (2009) and Permetti *et al.* (2007) suggest mixed systems that employ surfactants, and could offer advantages for structuring of oilcontinuous emulsions (and in specific cases water continuous emulsions), as many food products are emulsions.

It would be useful to know how alternative "hosts surfactants" might work with other surfactant combinations (Fujiwara *et al.*, 2000; Sakamoto *et al.*, 2003, 2004). The presence of interfaces, as in emulsions, will influence the creation of building blocks as required for oil structuring. Ishizuka *et al.* (2009) reported that surfactant molecules in water and other solvents can form various self-assembled structures such as micelles and liquid crystals, due to their hydrophobic interaction. The authors found micellar shapes could form varied spherical, to worm-like structures, depending on composition, temperature and other factors. These micelle formations grow to form aggregates and behave like polymers, becoming highly viscoelastic and can entangle each other (Duffy *et al.*, 2009). Therefore, translating these structuring options to emulsions will likely necessitate reformulation. This suggests that rather than focus purely on single components, or perhaps mixed bulk organogel systems, investigation into real systems where aqueous phases are employed could provide useful information (Permetti *et al.*, 2007; Tanaka *et al.*, 2009).

In the case of a given interfacial emulsifier concentration, temperature, and shear rate, the surface of water droplets will be optimally or sub-optimally covered, especially in the context of HIPREs. Explaining these mechanisms could be problematic, in that laboratory scale techniques using standard methods could be limited because of their inability to provide data whilst under true dynamic conditions.

During isothermal conditions, the mechanical orientation of TAG and non-TAG structures and stabilisation could be critical, especially where, for example, TAG structures in themselves do not exhibit polar behaviour. However, at a certain surfactant concentration, the TAG crystals become more polar in behaviour because the surfactant is adsorbed to the TAG surface which theoretically produces more rigid and uniform structures. Evidence suggests that at certain concentrations and ratios of specific surfactants (template additives), the surface of water droplets is more optimally covered because of faster induction of heterogeneous nucleation to

form molecular aggregates, which act as a template for nucleation.

Through use of SR- μ -SAXD microscopic analysis of the lamellar plane directions and structural domains could also be performed which might provide a deeper insight into the emulsion crystallisation mechanics.

Understanding how to measure mechanical viscoelastic properties of structurant interactions, both in model and real-time dynamic measurements, for example, UVP-PD, will be necessary (Permetti *et al.*, 2007; Povey *et al.*, 2007; Schaink *et al.*, 2007; Young *et al.*, 2008; Arima *et al.*, 2009; Ishizuka *et al.*, 2009; Ojijo *et al.*, 2009; Rogers, 2009; Wassell *et al.*, 2010).

CONCLUSION

This review has looked at several systems considered able to structure low saturated fat-based systems and which in themselves could also have emulsification properties. The presence of interfaces, as in emulsions, will interact with the creation of building blocks as required for oil or fat structuring. Although many food products are essentially emulsions, interest in the structuring of oil-continuous emulsions (and in specific cases water-continuous emulsions) will not be straightforward, especially where some more novel structuring materials are used either wholly or partially to replace traditional structurants.

In attempting to reduce the degree of saturates in food systems, it will be necessary to observe effects on mixed structurants and to analyse this relationship when cosurfactant structures are used and how this may influence interfacial film thickness, strength and flexibility.

Understanding how to measure mechanical viscoelastic properties of structurant interactions both in model and real-time dynamic systems will be necessary to account for diffusion, orientation and self-assembly mechanisms. In the case of exploring how novel structures behave within W/O or O/W emulsions, it will be important to understand how interfacial active emulsifiers will behave at these surfaces to form heterogeneous structures.

Clearly, greater understanding of the role of these factors will require further investigation.

The authors consider that the answers to these problems are most likely to be achieved through three main routes; (1) combining traditional techniques with novel structurant technology; (2) developing and validating in-line dynamic measurement techniques; and (3) investigation of emulsion systems, as opposed exclusively to single phase model systems.

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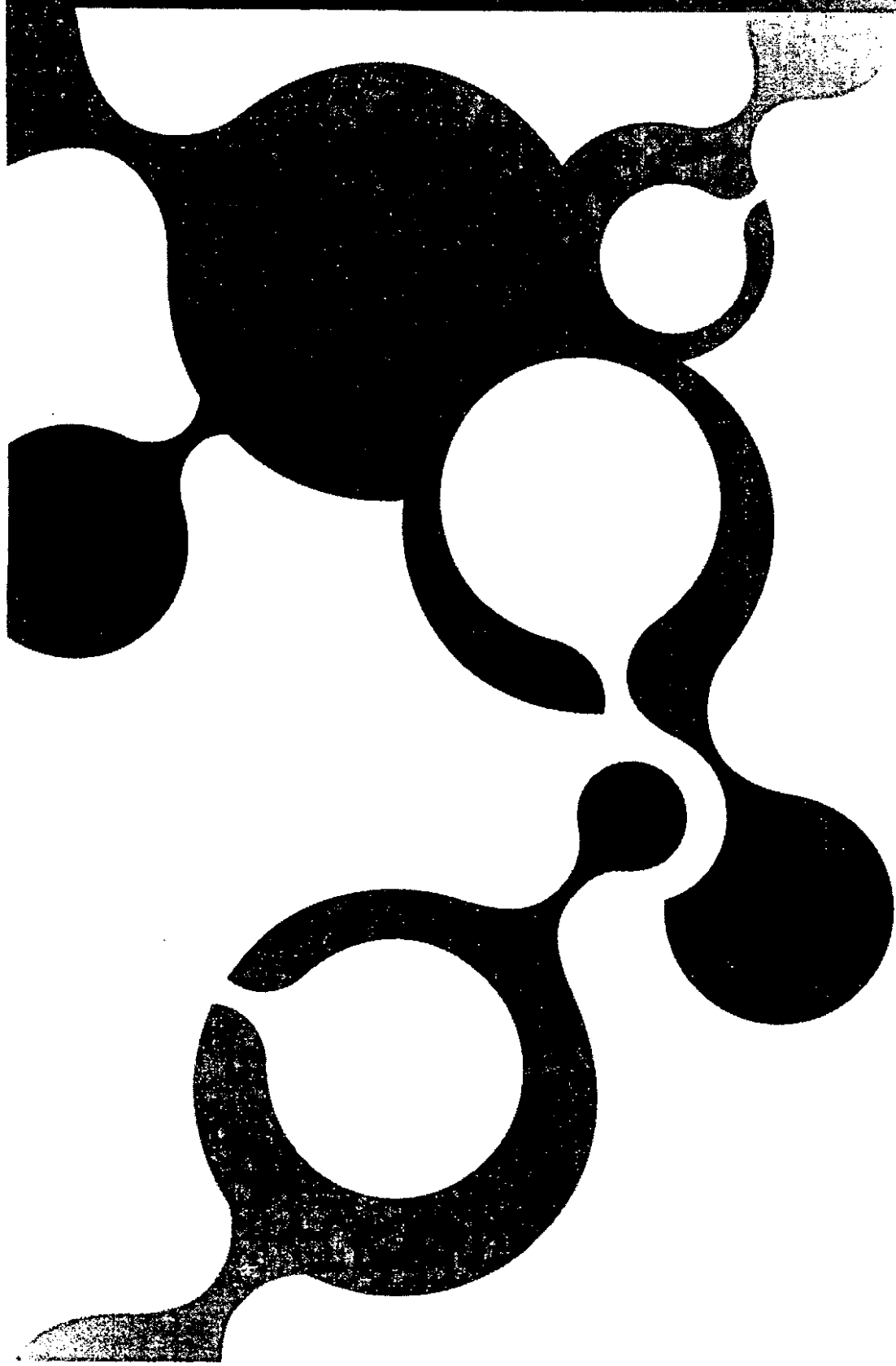
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DANISCO

First you add knowledge ...

Towards a multidisciplinary approach to structuring in reduced saturated fat-based systems – a review

DANISCO



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SUMMARY

Although many food products are essentially emulsions, interest in the structuring of oil-continuous emulsions (and in specific cases water-continuous emulsions) is intense, particularly to meet the continuing challenge of reducing the degree of saturates in food systems. Consequently, it is necessary to observe the effects of structurants and to examine their impacts on current food systems. This is especially the case where novel structuring materials are used to wholly or partially replace traditional structurants. A multidisciplinary approach is discussed encompassing traditional and novel mechanisms considered able to structure within low saturated fat-based systems and which in themselves could also have emulsification properties. The presence of interfacial compositions as in emulsions requires a crucial understanding of the interactions within these compositions for the creation of building blocks in oil or fat structuring. Where a co-surfactant structure may be used, together with novel structurants, for example, wax esters, phytosterols, it is necessary to understand how these may influence interfacial film thickness, strength and flexibility. Understanding how to measure mechanical visco-elastic properties of structurant interactions both in model and real time dynamic measurements will be necessary to account for diffusion, orientation and self-assembly mechanisms.

This review discusses combining traditional techniques with novel structurant technology; developing and validating dynamic measurement techniques; and investigation of real systems as opposed to purely model systems.

INTRODUCTION

The issue of *trans* fatty acids (TFA) replacement has been the subject of intense discussion and debate within the food industry as well as in the clinical field, with

a strong focus on reducing total saturated fatty acid content for health reasons (Berger, 2009; Fletcher, 2006; FSA, 2008). Achieving this is not simple, because many consumers expect particular textural properties in a given food product. The aroma, texture and mouth sensations experienced when consuming these foods are strongly dependent on their fat content and can eventually shape dietary choices in the long term (Drewnowski *et al.*, 1989; Drewnowski & Almiron-Roig, 2009). Thus, the idea of reformulating familiar foods which historically contained significant amounts of fats and oils (and usually contain significant levels of saturated fat) into lower fat versions is challenging not only technologically but also from a consumer acceptance point of view. Research into consumer perceptions of a new food product is often compared with memorised experience from a similar consumed food. Consumers may tend to conclude their decisions on the basis of their memory of a food, and not on the basis of their actual perceptions (Mojet & Koster, 2005; Morin-Audebrand, 2009).

It is reported that the consumption of TFAs may raise low-density lipoprotein (LDL) cholesterol levels, and lower high-density lipoprotein (HDL) cholesterol levels, thus contributing to atherosclerosis and an increased risk of apoplexy (European Food Safety Authority, 2004; FSAI, 2008; Gidding *et al.*, 2009). However, there is still debate as to the relevance of the intake of TFA from naturally occurring ruminant sources (Willett & Mozaffarian, 2008) and of the importance of saturated fats. McNeill (2009) clearly showed that despite a large body of epidemiological data being generated over the last two decades in respect of their adverse effects, there are also apparently certain important positive effects. Thus the effects of saturated fats on cardiovascular disease are complex.

Legislation, and literature (Dubinsky, 2008; Mozaffarian *et al.*, 2006; Stender & Dyreberg, 2003; Stender *et al.*, 2006; WHO, 2007) state that *trans* fatty acids should be removed from food, but current research (Stender *et al.*, 2009) suggests that this is insufficient in terms of creating healthy foods. Removal of, or at least drastic reduction of, not only *trans* containing fats, but all saturated fats is also required (Merchant *et al.*, 2008; SACN, 2007; Wassell & Young, 2007; Young & Wassell, 2009).

Realising the legislative requirements of governments, and consumer expectations for the food industry, is a tremendous challenge (Pernetti *et al.*, 2007). Achieving this balance of adequate structure in fat-based food systems whilst lowering the total saturated fatty acid content is a major objective of the food ingredient industry which remains elusive. For well over a decade the issue of *trans* fatty acid removal from bulk fat based systems has been the main focus of research in this field (Wassell & Young, 2007), and in some countries remains so (Benincá *et al.*, 2009; Willson, 2009), for example, Brazil and USA, respectively. However, the predominant global attention is in reducing total saturated fats, which of course includes *trans* fats (FSAI, 2008; L'Abbé *et al.*, 2009; Rogers, 2009; Wassell, 2010; Willett & Mozaffarian, 2008; Willson, 2009; Young & Wassell, 2008). However, whilst the problem is global: for some cases in emerging economies, the degree of importance placed on providing food products with lower *trans* and saturated fats has taken lower priority (Pérez-Ferrer *et al.*, 2010). Whilst there is general agreement that total fat levels should be reduced, there is disagreement as to the best route (Montague-Jones, 2009). Talbot *et al.* (2007) advocate the use of saturated fats preferably from natural sources. Others agree suggesting for example, that movement to reduce dairy food consumption

(and hence saturated fatty acids) irrespective of the nature of the dairy product should be made with caution (German *et al.*, 2009; SACN, 2007). Marangoni (2007) suggests that the use of saturated fat in the absence of *trans* fats is not a solution. As a result, alternative mechanisms for providing structure without saturated and/or *trans* fats to allow edible oil structuring have found increasing attention (Bot *et al.*, 2009b; Hughes *et al.*, 2009; Rogers, 2009).

Recent studies explore the different strategies including, lipid crystal engineering (Schäink *et al.*, 2007); phytosterol systems (Bot *et al.*, 2009b); organogel-based emulsion systems (Duffy *et al.*, 2009) and wax technology to form "lipo-colloid" structures (Shigemori, 2006). A comprehensive discussion of current possibilities is proposed by Perneti *et al.* (2007), who state succinctly that finding alternatives to traditional triacylglyceride (TAG) structuring whilst maintaining healthy properties, versatility and performance, is a tremendous challenge.

The aim of this review is to highlight the current state of the art, and propose a multidisciplinary-based approach to achieving the goal of providing structure for low saturated TAG systems and characterising these by means of new analytical approaches, which may include measurements within both static (Arima *et al.*, 2009; Tanaka *et al.*, 2009) and dynamic conditions (Wassell & Young, 2007; Young *et al.*, 2008; Wassell *et al.*, 2010).

TAG STRUCTURING

Traditionally, where TAG structuring is used, hard fractions and/or modified hard stocks composed largely of saturated fatty acids, also contained significant amounts of *trans* isomers (Kodali, 2005; Flöter & van Duijn, 2006; Podmore, 2008; Wassell, 2010).

Modification techniques and even the simple selection of alternative oils, for example, rice bran oil, shea, moringa, allanblackia (Lalas & Tsaknis, 2002; Most *et al.*, 2005; Garcia, 2006; Ghosh, 2007), have demonstrated the possibility of minimising and controlling the *trans*/saturated content

of oil blends and to successfully formulate alternative hardstocks (Abdulkarim *et al.*, 2005; ACNFP, 2006; Bell *et al.*, 2007; Annon, 2008; MacKenzie, 2008; Lerma-García *et al.*, 2009; Mayamol *et al.*, 2009).

The combination of techniques leads to a greater variety of hardstocks with a wider range of physical properties such as solid fat content and melting profile. This is particularly important for fats from which a specific performance is expected. Exclusive focus on the physico-chemical aspects but neglecting the fat's required functional role within the final application leads to other problems. Matching the physical properties of a commercial fat blend to a specific application is normally based on solid fat profile, melting point and textural qualities. Subsequently, the commercial fat blend's plastic range might be expected to be within a given tolerance (Young & Wassell, 2007; Wassell, 2010). Ultimately, the reason for this is to fulfil performance phenomena such as creaming, crystallisation and emulsification, which also need to be considered. Therefore, fatty acid composition, polymorphism and process conditions can not be ignored. Concentrating exclusively on the fat phase does not necessarily address the whole challenge in the case of reducing total saturates, for example, addition of a water phase, creating an emulsion, which automatically reduces the fat content in the final application. However, to effectively pursue this strategy often requires balanced emulsifier technology and possibly the use of other additives, and even subsequent redesign of the final food product may be necessary (Wassell & Young, 2007). It is known that the composition, polymorphism, solid fat content and microstructure of TAGs all play a crucial role in the structure of lipid-based products (Christie, 1982; Timms, 1985; Garti & Sato, 1988; Larsson, 1994; Narine & Marangoni, 1999; Hartel, 2001; Rogers, 2009). The major advantage of TAG structuring is the diversity of the molecules and molecular configurations, which allows for the physical properties to be tailored to the final application by changing the chemistry of the molecules or by modifying the processing conditions,

enabling production of solid and semi-solid fats (Bailey's, 2005; O'Brien, 2009).

HYDROGENATION

Hydrogenation or partial hydrogenation processes, which have been commonly used in the modification of oils for food product formulations, are able to deliver specific, desired melting behaviours for fat blends (Hamm & Hamilton, 2000; Gunstone, 2002; Podmore, 2008; Dijkstra, 2009). The proportion of fatty acids which can be changed through hydrogenation is classified as unsaturated fatty acids, having one (monounsaturated), two or three (polyunsaturated) double bonds. These types of fatty acids usually have the *cis* configuration, that is, the hydrogen atoms with respect to the double bond are on the same side of the molecule. Fully saturated fatty acids do not contain double bonds and are least reactive chemically (O'Brien, 2009).

Addition of hydrogen atoms across the unsaturated double bonds, causing saturation of the TAGs, causes more rigid structures because of the new molecular configurations. Apart from removing or shifting the double bond, the same process can also cause the *trans* configuration associated with negative health effects (Stender & Dyreberg, 2003). Fatty acids specified as being in the *trans* configuration have the hydrogen atoms on the opposite sides of the molecule, and the molecule assumes a nearly linear configuration similar to saturated fatty acids. Hence *trans* fats behave more like saturated fatty acids. Partial hydrogenation, which is carried out to alter the plasticity and functional properties of a fat, produces several *cis* and *trans* fatty acids from intramolecular rearrangements. Irrespectively, any increase in saturation results in higher melting point of the TAG, and therefore, is more solid at room temperature (Foster *et al.*, 2009). Importantly, as mentioned during the introduction, not all *trans* fatty acids are produced by commercial hydrogenation (SACN, 2007; German *et al.*, 2009). Indeed there is intense debate where dairy fats are concerned and a need to differentiate between effects of hydrogenated and naturally occurring *trans* fats (Kummerow,

2009). Options to reduce the *trans* levels during the hydrogenation process of edible oil have been investigated (Beers, 2007).

INTERESTERIFICATION

In view of the limited ability of solidifying "natural" TAGs to create certain structures, other naturally occurring hardstock components, that is, from palm oil are used. The basic principles of interesterification were first documented by Fondu & Willems (1969) and they described a process which resulted in the rearrangement of the distribution of the fatty acids either chemically or enzymatically, within and between the triglycerides. Consequently, the fatty acid distribution is altered but the fatty acid composition remains unchanged – this rearrangement can occur either in a random or controlled manner (Yusoff & Dian, 1995). The net effect of rearrangement leads to production of oils that require a certain semi-solid-plastic range having different levels of structure, each influencing the macroscopic properties of the material (Tang & Marangoni, 2006a; Ribeiro *et al.*, 2009).

FRACTIONATION

The controlled crystallisation of TAGs can result in the separation (fractionation) of a solid phase (stearin) and a liquid phase (olein). In turn, these can be further fractionated (van Duijn *et al.*, 2006).

Essentially, the process of fractionation consists of crystallisation to produce solid crystals in a liquid matrix, and separation of the crystals from the liquid matrix (Timms, 1997). Fundamentally, fractionation processes work to the following principles: complete melting of the fat, slow cooling, gentle or no agitation to encourage the development of large crystals and separation into liquid and solid fractions with differing physical and chemical compositions (Timms, 2005). An excellent review by Timms (2005) discusses the different fractionation methods, and Dijkstra (2009) provides information on recent developments not just in fractionation, but reviews edible oil processing generally.

Palm is probably the most important oil in terms of fractionation because of its

unique fat profile (Sahasranamam, 2005) which can be broken down into individual fractions (Timms, 2007). Another term used for fractionation is winterisation, and is essentially the process of removing wax esters and high melting TAGs at lower ambient temperatures, and still has modern use today particularly for oils liquid in the ambient temperature range (MacKenzie, 2008).

Fractionation has been shown to be useful in the replacement of some emulsifiers – specifically highly saturated emulsifiers, with low iodine values, which are difficult to replace with non-hydrogenated emulsifiers. To supply emulsifiers, which have the same physical/chemical characteristics as the widely used hydrogenated types, but preferably, in a non-hydrogenated form is challenging.

It is the more saturated, and preferably the fully saturated monoglycerides which are able to assist in both emulsification and promote crystallisation. An example is in the preparation of emulsions for industrial margarines, which typically require use of simple monodiglycerides. Bech *et al.* (2008) describe a method of preparing a non-hydrogenated emulsifier having substantially no *trans* carbon-carbon double bonds, and further discusses other surfactants which are built on "natural"

feed stocks, which may be fractionated, to give remarkably low iodine values; an indicator of the degree of saturation.

Talbot *et al.* (2007) favour fractionation for design and control of the fat blend due to it containing a significant portion of high melting TAG's (Lida & Ali, 1998; Sundram, 2005). Timms (2005) neatly summarises the whole mechanism and comments that with the decline in hydrogenation, interesterification has seen a renaissance, although it is only partially able to replace hydrogenation. Additionally, interesterification suffers from the "chemical"-process image and environmental drawbacks of hydrogenation. Therefore, fractionation, a purely physical process, more adequately satisfies today's increasing environmental and health concerns.

NON-TRADITIONAL STRUCTURANTS

As TAGs are responsible for the network structure in traditional systems, it is difficult to entirely remove saturated fats without compromising some sensory and physical characteristics. Alternative structurants for discussion are listed in figure 1. Several reviewers acknowledge the necessity to revisit some of the traditional solutions and couple these with the use of novel materials, because it is unlikely that one novel structurant, for example, mixture

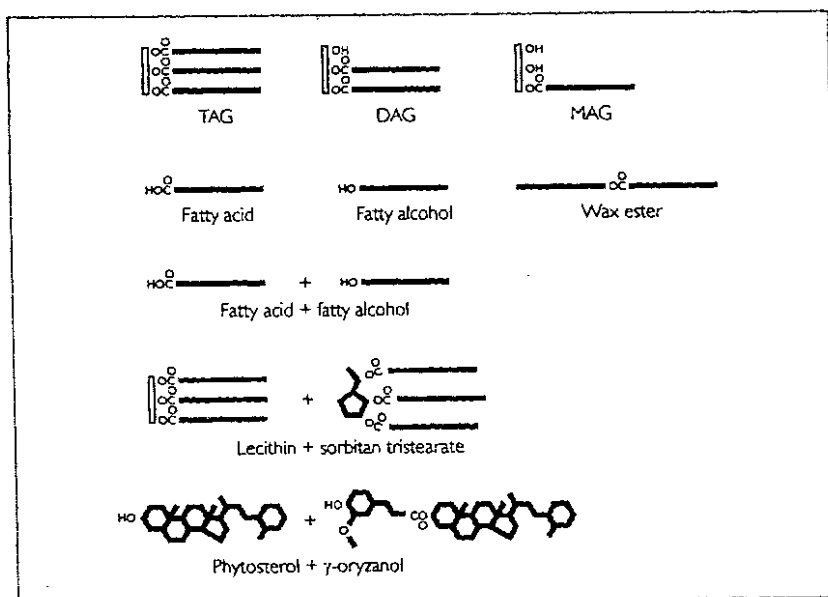


Figure 1. Schematic representation of a number of structurants for TAG oil phases (Permetti *et al.*, 2007).

of phytosterols and oryzanol could satisfy all requirements. Rather, this mixture in a TAG-based, water-in-oil emulsion with a surfactant is more realistic (Pernetti *et al.*, 2007; Schaik *et al.*, 2007; Bot *et al.*, 2009b). Therefore, textural properties to which consumers are accustomed may not be achieved through singular techniques. It is likely that synergies obtained through combining disciplines, understanding of thermodynamic mechanical properties and critical design of real systems, will play a vital influence (Fomuso & Akoh, 2001; Pernetti *et al.*, 2007; Duffy *et al.*, 2009; Hughes *et al.*, 2009; Rogers, 2009). Therefore, it is suggested that a multidisciplinary approach to the study, design and possible solution of the problem is necessary (Wassell & Young, 2007; Young *et al.*, 2008; Wassell, 2010).

TAG

Apart from that discussed in the TAG structuring section, Higaki *et al.* (2003) observed gel-like behaviour in TAG mixtures of fully hydrogenated rapeseed oil with behenic acid concentrations of 1.5–4.0 wt%. Rapid cooling and heating to final temperature were necessary to achieve gel-like behaviour, whereas simple cooling without a cooling/heating procedure did not form a gellike fat mixture. This is attributed to cooling rate, agitation and degree of supercooling, control the rate of crystal growth and thus crystal size and crystal agglomeration, which affect the textural and melting properties of the fat product (Humphrey & Narine, 2004). Importantly, Higaki *et al.* (2003) was able to influence polymorphism by adjusting thermal treatment and tempering, to achieve a β -gel without waxes, or other emulsifier additives. The subject of polymorphism is not discussed in any detail within this review, and good explanations are provided within the literature (Hernqvist, 1984; Sato, 2001).

Mentioned in the previous section, Pernetti *et al.* (2007) discusses several mixed structurant systems could benefit from utilising TAGs with novel structurants under specific process conditions, a multidisciplinary approach. This will subsequently be enlarged upon during this discussion

(Wassell & Young, 2007; Young *et al.*, 2008; Hughes *et al.*, 2009; Wassell, 2010).

DAG

Pernetti *et al.* (2007) note that surprisingly little attention has been given to structuring using diacylglyceride (DAG or diglyceride), and the authors cite dipalmitin and distearin as forming crystalline networks in a similar way to those formed by TAGs. These gel formations are slightly softer than TAG crystal networks of similar concentration. Indirectly, the reduction and influence of diglyceride content can also play a positive effect as a β -stabiliser (Hernqvist & Anjou, 1983; Cheong *et al.*, 2009), which has not really been exploited (Kristensen *et al.*, 2005). The reduction of diglycerides in palm oil rich blends, can lead to an increase in the total solid fat content. Thus, it is possible to produce similar viscoelastic profiles in products, normally associated with a higher degree of saturated fatty acids. Examples are: margarine, salad dressing products, nutritional bars, muffins, brownies, breads, cookies, doughs and batters for baked goods (Boice *et al.*, 2003; Sikorski, 2005; Kristensen & Wassell, 2006).

MAG

Monoacylglycerol (MAG or monoglyceride) components are able to structure both lipid and aqueous phases (Marangoni, 2007; Rogers, 2009; Rush *et al.*, 2009). MAGs are thought to form reversed bilayers in TAG oils. Ojijo *et al.* (2004a,b) investigated the formation of stable network structures through the cooling of mixtures of various concentrations of monoglycerides and vegetable oils. Mechanical hardness of olive oil/MAG gel networks was investigated. A given minimum monoglyceride volume fraction was necessary for formation of a gelled network. The onset of the gel network or structure formation was indicated by a change in the value of the elastic modulus, whilst network hardness increased with increase in MAG content. High cooling rates led to low final elastic modulus values but harder networks, whereas slow cooling rates gave the reverse. Maximum gel network development occurred with moderate shear rates, thereby highlighting

the fact that the physical and functional characteristics of such products, in this case, depend on processing conditions, cooling rate, shear and presence of co-surfactants (Ojijo *et al.*, 2004b; Pernetti *et al.*, 2007; Davis *et al.*, 2009; Hughes *et al.*, 2009; Krabbenhoft *et al.*, 2009; Rogers, 2009; Tippetts & Martini, 2009).

Novel structurants

Hughes *et al.* (2009) report that a number of organogelator systems have the ability to gel edible oils at very low concentrations (~0.5–2.0 wt%), and apart from those previously mentioned, include network-forming edible oil structurants: TAGs, DAGs, MAGs. Murdan *et al.* (1999) discuss sorbitan mono-stearate and Gandolfo *et al.* (2004) and Schaik *et al.* (2007) discuss mixtures of fatty acids and fatty alcohols. Combinations of lecithin and sorbitan tri-stearate, phytosterols and oryzanol have also been reviewed (Pernetti *et al.*, 2007). Other organogelators or mixtures are well-known for their ability to structure in edible oils: 12-hydroxystearic acid (Rogers *et al.*, 2007, 2008a,b, 2009), ricinelaidic acid (Wright & Marangoni, 2006), candelilla wax (Toro-Vazquez *et al.*, 2007), mixtures of β -sitosterol and γ -oryzanol (Bot & Agterof, 2006). Rogers *et al.* (2009) also show that sphingolipids, like triacylglycerides, can exhibit variability in the fatty acid chain length. These are able to form long thin fibre structures, creating greater surface area and thereby stabilising more polyunsaturated liquid oil (Christie, 2010).

Irrespective of the network composition, organogels have numerous potential different functionalities in food products (Duffy *et al.*, 2009), and are not limited to oil mobility and migration, the replacement of saturated and trans fats, and the stabilisation of emulsions (Pernetti *et al.*, 2007; Rogers, 2009). Network forming modified polymers are known to have dual affect as structurant and surfactant capability at oil water interfaces, but these are usually non-edible applications, and therefore not within the scope of this review.

Other food grade polymers include cellulose derivatives including chitosan (Pszczola, 2006; Rietberg & Marangoni,

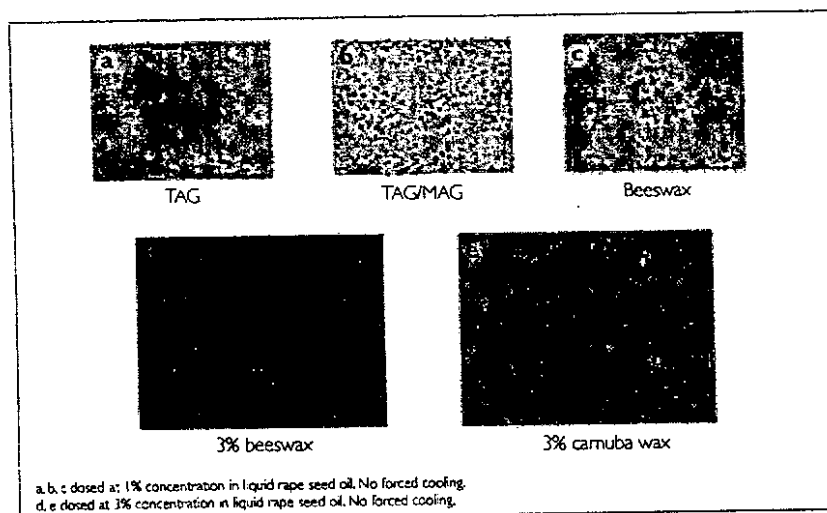


Figure 2. Waxes compared with traditional TAG and monoglyceride (MAG) (M. Nielsen, unpublished data).

2009), however, the use of these materials for edible oil structuring is rare due to restrictions on modifications for food use (Permetti *et al.*, 2007) and therefore applications tend to be associated to oil-in-water applications because cellulose derivatives such as cyclodextrins must be fully hydrated for functionality (Cui & Wang, 2006).

Waxes/fatty acids/phytosterols

Experimental application of wax in peanut butter provides an example of a multidisciplinary approach, where a naturally slow crystallising beeswax is used to replace traditional TAG based hardstock. A "lipocolloid" – like network is formed, with efficient needle shaped structures, rather than spherical shaped particles (Permetti *et al.*, 2007). Waxes compared with traditional TAG and MAG solutions are shown in figure 2. In liquid oil, similar yield stress values can be achieved using lower inclusions than typical TAG or MAG concentrations (M. Nielsen, unpublished data). Mellema (2009) studied co-crystallisation of beeswax and various vegetable waxes with sterols and reported that rice bran wax, sunflower wax and jojoba can increase crystal events in a formulation. Furthermore, Mellema (2009) highlighted the benefits of heRP70 (fatty acid composition: C16:0–5%, C18:0–40%, C20:0–9%, C22:0–43% with more than 99.5% total saturated fats), reporting the replacement of beeswax with combina-

tions of heRP70, sunflower oil, or jojoba wax also significantly increased the amount of crystalline material in the formulation. This was attributed to improved solubility of the sterols. This provides scope for combining traditional and novel solutions (Permetti *et al.*, 2007). Toro-Vazquez *et al.* (2007) established the oil structuring property of candelilla wax in safflower oil at concentrations of ~1 wt% and higher. Kodali (2009) also reports Ricebran wax being able to stabilise other long chain polyunsaturated oils.

Dassanayake *et al.* (2009) report network formation of rice bran wax crystals and show organogel properties occurred more rapidly, coinciding with temperatures of crystallisation than that of the mixtures of carnauba wax and candelilla wax in olive oil. The same authors also observed a low concentration of carnauba and candelilla wax was necessary to form an organogel in olive oil at 4 and 2 wt%, respectively. Gel structures formed soon after rice bran wax crystallised, whereas a time delay was observed between the organogel formation and wax crystallisation of carnauba wax and candelilla wax, demonstrating rice bran wax has good organogelforming properties. The quicker gelation in the rice bran wax system was attributed to comparatively longer fibrous crystals of rice bran wax which form gelator networks efficiently entraining the liquid oil.

Martini *et al.* (2008) discuss two different crystal populations when testing sunflower oil wax (SFOw) in anhydrous milk fats (AMF) and suggest the presence of two different populations of crystals. This could be attributed to differences in the molecular weights of SFOw and AMF, where the AMF at high temperatures crystallise very slowly forming large agglomerates. These authors found that the addition of SFOw could decrease the induction time of crystallisation, promoting crystallisation, especially towards high temperatures. Dassanayake *et al.* (2009) reported the presence of different components within the wax, which seemed to have a profound effect on the crystal habit of the plant wax-vegetable oil organogels. Conditions of organogel preparation (e.g. degree of agitation, cooling rates and storage conditions) were likely to influence crystal morphology of the gelators.

Mellema (2009) investigated methods for solubilising sterols, which in themselves form structures, but can be difficult to incorporate into TAG systems (Permetti *et al.*, 2007; Hughes *et al.*, 2009; Rogers, 2009). Mellema (2009) found that mixing molecularly similar waxes, including ursolic acid (found within apple waste) facilitated the incorporation of sterols. Bhagga *et al.* (2002) showed that by adding a blend of ursolic acid and oleanolic acid to a fat *per se* or to a fat in a food product, the crystallisation rate of the fat could be increased concomitantly with the hardness of the fat composition. Furthermore, it was found that the addition of the ursolic acid/oleanolic acid mixture also improved other properties of the total composition, such as oral mouthfeel, heat resistance, and aeration properties. Combining waxes and specific fatty acids, might be suitable, because of their similar hydrophobicity to sterols and their typical plasticity, which allows a structural "flexibility" for the sterols to fit into a crystal network (Mellema, 2009).

Organogel – phytosterol emulsions/ 12-hydroxystearic acid

Little is known about the structures formed in specific organogels and how these structures might behave at the emul-

sion interface. Duffy *et al.* (2009) studied oil-in-water organogels based on edible oils and specific mixtures of phytosterols, in an attempt to describe and understand micro-structural features, prepared using basic processing conditions. They showed that long thin crystals are formed extending out of the oil phase into the continuous water phase. These emulsions of phytosterol-based organogels in an aqueous solution formed with the presence of emulsifiers and resulted in the formation of small emulsion droplets; internal oil droplet structure was not studied. Schaink *et al.* (2007) showed that lipid crystal engineering using mixed crystals offers the prospect of obtaining harder organogels with less structurant. A possible application of this type of structurant mixture is the replacement of saturated fats in a broad range of water-in-oil products. For these applications, it is important to know whether the mixed crystals also contribute to the visco-elastic properties of W/O and O/W emulsions that are made using these structurants. Observing and explaining these effects is of technical relevance and should be investigated. Schaink *et al.* (2007) suggested that it would be interesting to combine different approaches in order to obtain an insight into the mechanism of organogel formation, which may lead to improved understanding of the polymorphism and crystal formations resulting from mixed components. Ishizuka *et al.* (2009) reported that surfactant

molecules in water and other solvents can form various self-assembled structures such as micelles and liquid crystals, because of their hydrophobic interaction. The micellar shapes can vary from spherical to worm-like structures, depending on composition, temperature and other factors. When micelles grow to form aggregates and behave like polymers, becoming highly visco-elastic, they may entangle each other.

"Self-assembled fibre networks" (SAFiN) are well reported (Pernetti *et al.*, 2007; Rogers *et al.*, 2008a; Rogers, 2009) and spontaneously form fibres, capable of structuring the oil phase. Duffy *et al.* (2009) report systems able to form structure in the aqueous phase, and it has been confirmed (Bot & Agterof, 2006; Bot *et al.*, 2008; 2009a) that β -sitosterol – γ -oryzanol fibril systems are quite unique as they are one of the few combinations capable of forming fibril structures in both aqueous and oil systems. Both Duffy *et al.* (2009) and Ishizuka *et al.* (2009) report formation of micellar tube-like structures (figure 3) in the aqueous phase. They found their formation to be time and temperature dependent and they concluded that a diffusion-based mechanism might occur, in which the sterols or sterol containing features move and rearrange from the lipid phase into the aqueous phase. Duffy *et al.* (2009) show that sterol solubility in edible oil is further reduced with the transition from a pure organogel system

to an organogel-based emulsion system, and explained that in hot dry vegetable oils sterols are reasonably soluble, but this decreases in oil saturated with water (Jandacek *et al.*, 1977; Duffy *et al.*, 2009). This has implications, because depending on the presence of another co-structuring material, for example, lipid; it may affect diffusion, and integration kinetics differently (Povey *et al.*, 2007).

The above observations have significance not only to the understanding of how these structurants are behaving in model systems but also to their behaviour in "real" emulsions. This raises the question of how combinations of such structurants may perform both thermodynamically and mechanically at the interfaces of O/W or W/O emulsions (Bot *et al.*, 2009a,b). Thus the question of phytosterol solubility and its potential structuring ability requires further investigation. Understanding how to measure mechanical visco-elastic properties of structurant interactions both in model and real time dynamic measurements (Povey *et al.*, 2007; Ishizuka *et al.*, 2009; Ojijo *et al.*, 2009) will therefore become increasingly necessary (Pernetti *et al.*, 2007; Schaink *et al.*, 2007; Arima *et al.*, 2009; Rogers, 2009; Tanaka *et al.*, 2009; Young *et al.*, 2008).

Application of alpha (α) polymorphic tending emulsifiers (Stauffer, 1999) in liquid vegetable oil to form a soft gel mixed into the aqueous phase has been reported (Wassell, 2006a,b). The α crystalline form is more flexible than the rigid beta (β) crystalline form and rearranges more easily during heating cycles. The former establish a physical film at the interface of the oil droplets and prevent inhibition of foam formation with relatively low levels of total oil/solid fat. This provides a significant reduction of total saturates (Wassell & Young, 2007). A suppression of the solid fat content is also observed with additions of between 5 and 10 wt% mixed, fully hydrogenated surfactants (Wassell, 2006a,b). Suppression, and time delay of solid fat content is also reported by Hughes *et al.* (2009) where addition of 2% w/w 12-hydroxystearic acid (12-HSA) to a model filling (60:40 canola

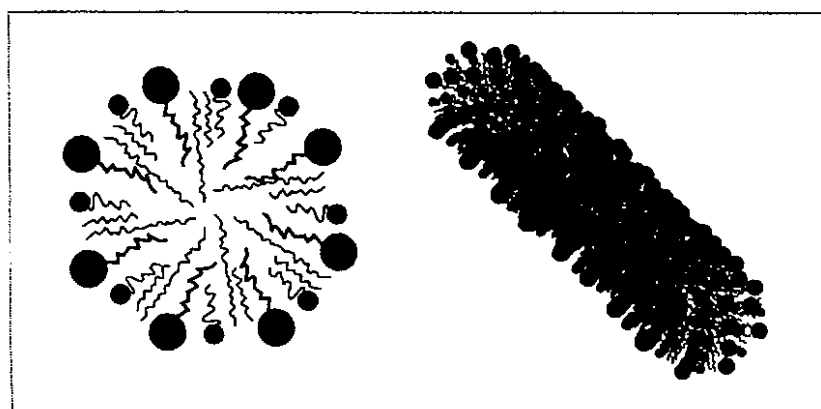


Figure 3. Schematic diagram (hypothetic model) of the ordering of the two sterol species with triacylglycerides in a 10-nm tube structure. The molecules are drawn on scale approximately. Red γ -oryzanol, green β -sitosterol; "chair-model": triacylglycerides. The right image shows a schematic diagram of the tube structure; organisation of the sterols with respect to each other may be more random. Adapted from Duffy *et al.* (2009).

oil/interesterified hydrogenated palm oil) composite cream-filled confection, did not increase the solid fat content of the mixture. Isothermal crystallisation occurred at 20 °C. The authors explained that 12-HSA is a high melting point lipid component, and therefore, theoretically the SFC of the mixture would be expected to increase proportionally with its addition. However, its inclusion did not translate to a higher SFC and therefore addition of 12-HSA either delays or slows normal crystallisation (Hughes *et al.*, 2009).

Hughes *et al.* (2009) proposes potential food applications of edible oil organogels and emulsions, reporting the complexity of network formation and bonding interactions, and is considered difficult to design systems or predict which organogelators will work with a particular solvent, therefore immobilised water droplets within a continuous gelled oil phase were investigated. Hughes *et al.* (2009) suggest that given certain formulation and processing conditions, organogelled emulsions may have application as low-fat spreads or to control the release of both hydrophilic and hydrophobic bioactive (probiotic) compounds (Hughes *et al.*, 2009).

Hughes *et al.* (2009) report the potential application of water-in-gelled-oil emulsions, where addition of typical food grade emulsifiers (i.e. Span 60 or Tween 80) drastically modified the textural properties which can negatively affect the ability of 12-HSA to gel oil. 12-HSA is not considered a food grade additive as it is derived from castor oil and is considered an irritant, although Rogers (2009) reports it as being an ideal compound for examining macroscopic changes in processing conditions. Others have recently investigated and studied the physico-chemical, self-assembling behaviour and potential of 12-HSA, to form tube like structures. Additions in excess of 30% of other lipids (saturated fatty acids), or phospholipids could be incorporated without negatively affecting structure (Fameau *et al.*, 2010).

Crystal habit modifiers and co-gelators
Recent publications have discussed the use of "crystal structure modifiers" (Garbolino

et al., 2005; Rousseau *et al.*, 2005; Pernetti *et al.*, 2007; Young *et al.*, 2008), addition of a co-surfactant (Foster *et al.*, 2007; Rogers, 2009), inclusion of an additive, accelerant (Katsuragi, 1999; Fujiwara *et al.*, 2000; Wassell *et al.*, 2010), or impurity (Awad & Sato, 2001, 2002).

Crystal structure modifiers are potentially interesting not only within traditional systems, but also within novel structures and mixtures (Pernetti *et al.*, 2007). Effects of, hydrophobic, adsorption properties of additives and template behaviour for acceleration of surface heterogeneous nucleation events have been studied (Awad & Sato, 2001, 2002; Cendeira *et al.*, 2003, 2005, 2006; Sakamoto *et al.*, 2003, 2004). More recently, the behaviour of unsaturated and saturated surfactants, their polymorphism, time temperature effects and advanced analysis (Arima *et al.*, 2009; Tanaka *et al.*, 2009) has provided information on the interactions of minor components (Vereecken *et al.*, 2009a) and crystallisation with and without water phase (Vereecken *et al.*, 2009b). Whilst all these observations are vital in providing understanding, it is also considered important to observe effects of mixed surfactant systems, and how these interactions influence their relative relationship in TAG and non-TAG mixtures (Pernetti *et al.*, 2007; Rogers, 2009). Investigation of the kinetic stabilisation of emulsions with low concentrations of continuous phase crystals (Rousseau *et al.*, 2005) found polymorphic form and morphology could be manipulated through a multidisciplinary approach, involving dilution, tempering regime and the presence of polyglycerol polyricinoleate (PGPR), under different crystallisation conditions – this being static vs. dynamic crystallisation (Young *et al.*, 2008; Wassell *et al.*, 2010). Rousseau *et al.* (2005) suggest liquid emulsifiers such as PGPR compared with surfactants such as saturated MAG are not as likely to influence crystal lattices, unless PGPR is combined with agitation conditions, where polymorphic transformation was retarded. However, static crystallisation in the presence of PGPR showed no differences. This aspect could be especially interesting to observe in the area of high internal-phase-

ratio emulsions (HIPREs) (Charteris, 2007) where interfacial film strength and mechanical flexibility will probably impact on final structures resultant from adsorption, diffusion and integration kinetics (Povey *et al.*, 2007).

Attempting to modify structures based on traditional, novel or a combination of these approaches, and especially where thermodynamic conditions are combined with co-gelators such as mixed surfactants, could lead to some potentially interesting physical properties (Hughes *et al.*, 2009; Rogers, 2009). Recently Bot *et al.* (2009b) investigated the importance of the composition of emulsions based on β -sitosterol and γ -oryzanol and found that increases in phytosterols led to an increase in firmness of the emulsion gel and that changing the ratio of β -sitosterol to γ -oryzanol proved more sensitive than previously observed for the pure organogels (Bot & Agterof, 2006). Bot *et al.* (2009b) also found it more critical to use a 40:60 β -sitosterol to γ -oryzanol weight ratio in order to achieve the optimal emulsion firmness. The effects of a number of minor ingredients, including MAGs, and make up of the water phase, were also investigated. The authors concluded that water activity is not important for the emulsion's properties, and found the addition of MAGs reduced droplet size and improved spreadability (Ritter *et al.*, 2005). Bot *et al.* (2009b) speculated that smaller droplets cause smaller "defects" in the organogel network, leading to firmer emulsion gels, but seem to be sensitive to the combination of cooling and shearing normally used in W/O emulsion processes. Hughes *et al.* (2009) found similar challenges when investigating organogel emulsions based on 12-HSA, though ultimately finding 12-HSA crystals to be dispersed evenly throughout the continuous oil phase and were not present inside or concentrated at the surface of the water droplets. Fairly large water droplets were formed, but these were stable (Hughes *et al.*, 2009). Both examples from Bot *et al.* (2009b) and Hughes *et al.* (2009) highlight room for further improvement in the emulsion preparation process. Research from studies within other disciplines (Peng *et al.*, 2009) may provide clues to the

formation of HIPREs using cholesterol derivatives as natural emulsifiers. HIPREs emulsions contain an internal phase volume of 70% (v/v) or greater, forming dispersed polyhedral structures, separated by thin films of continuous phase. These highly concentrated emulsions are also called "gel-emulsions" because of their visco-elastic behaviour (Peng *et al.*, 2009).

TECHNIQUES FOR INVESTIGATION

Most studies have been performed under isothermal conditions where observation of crystal behaviour is potentially quite different from that observed within a dynamic environment (Garbolino *et al.*, 2005; Janssen & MacGibbon, 2007; Maleky *et al.*, 2007; Povey *et al.*, 2007; Wassell *et al.*, 2010). Interactions of and between surfactants and their interactions as template structures, for example, in heterogeneous nucleation events (Fujiwara *et al.*, 2000), are not easily explained with typical measurements such as rate of crystallisation tests – static conditions – zero shear, and synchrotron (X-ray/DSC) tests – static conditions – zero shear (De Graef *et al.*, 2006; Pernetti *et al.*, 2007; Povey *et al.*, 2007). Improved understanding may therefore require the use of new techniques capable of observing and quantifying structural events in both static and under dynamic conditions (van Duynhoven *et al.*, 2005; Tang & Marangoni, 2006b; Arima *et al.*, 2009; Boodhoo *et al.*, 2009) and describing this relationship to their me-

chanical properties, for example, ultrasonic velocity profiling with pressure difference (LVP-PD) equipment allowing non-invasive in-line rheological measurement and synchrotron radiation microbeam small-angle XRD (SR-μ-SAXD) technique to more precisely observe microstructures of fat crystals (Prakash & Ramana, 2003; Mazzanti *et al.*, 2005; De Graef *et al.*, 2006; Maleky *et al.*, 2007; Pernetti *et al.*, 2007; Young *et al.*, 2008; Tanaka *et al.*, 2009; Wassell *et al.*, 2010). Determination and validation of methods will of course have to be approached with caution, in order to obtain an understanding of the potential diffusion or self organising mechanical properties leading to achievement of clear rheological behaviours (Morales-Rueda *et al.*, 2009). Nucleation events, which are likely to be heavily influenced by small quantities of high melting fats, acting as seed crystals, may be difficult to establish with current analytical techniques. The surface integration of molecules into growing crystals can similarly be upset by small quantities of impurities. Further, where fat crystallisation occurs within emulsions, this introduces additional complications (Himawan *et al.*, 2006).

DISCUSSION

Two themes seem to run through the literature; first, the necessity to move away from the addition of hard fatty material and substitute by alternative structure forming strategies. Second (related to first theme) is the need to

cause accelerated nucleation events through inclusion of a small amount of additive such as a surfactant. Such technology is well documented (Sakamoto *et al.*, 2003, 2004) and commercialised (Neddersen *et al.*, 2009). Therefore, given the aforementioned approaches, there are two areas for consideration; not just structure and assembly within the bulk oil, but the mechanism of structure at interfaces, for example, water-in-oil emulsions, and how the interface might be modified through surfactant-initiated surface heterogeneous nucleation to provide adequate structure, strength, and flexibility through a range of mechanisms (Povey *et al.*, 2007).

It is probable that there is a mechanism which could employ the use of "traditional" TAG-based structurants, coupled with novel structuring types (Pernetti *et al.*, 2007; Duffy *et al.*, 2009). For example, one of a range of previously discussed assemblies might be more efficiently optimised over shorter induction times, as a result of the inclusion of a material acting as an accelerant which might otherwise have been considered an impurity (Wassell *et al.*, 2010).

Structurants such as γ-oryzanol which work very well in bulk oil, may have limits within water-in-oil emulsions for products such as spreads, as they cannot provide the textural properties consumers are familiar with. However, modification of the thermodynamic driving force and addition

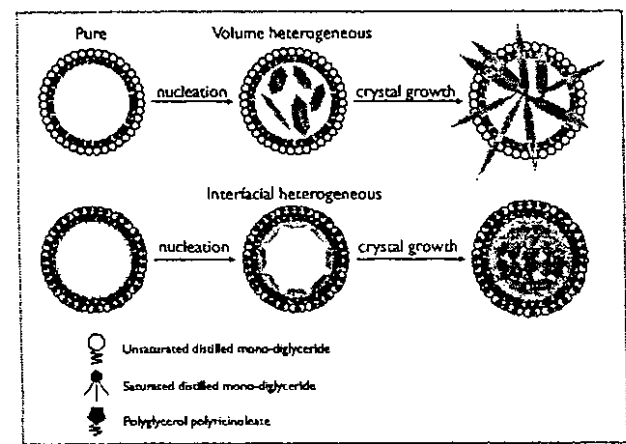


Figure 4. Heterogeneous crystallisation of O/W emulsion with additive. Adapted from Arima *et al.* (2007).

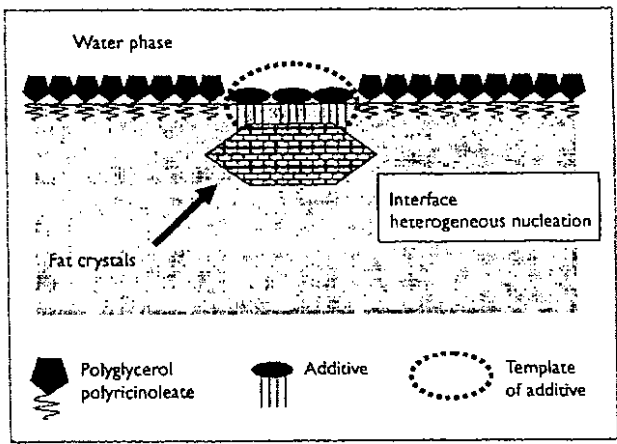


Figure 5. Additive to induce crystal nucleation, whilst retarding crystal growth. Adapted from Sato (2005).

of a co-surfactant (Foster *et al.*, 2007; Pernetti *et al.*, 2007; Rogers, 2009) could achieve nucleation through standard accelerated induction events with inclusion of a surfactant, for example, monoglyceride.

Among the components discussed by Rogers (2009), fatty acids, particularly long chain fatty acids, are ignored due to the negative health implications associated with traditional fat based networks. However, whilst the use of saturated TAG networks might not be a solution preferred by some (Marangoni, 2007), there are still unanswered questions regarding the use of surfactants derived from mixed, short or longer chain fatty acids (Vereecken *et al.*, 2009a; b). Pernetti *et al.* (2007) suggested that longer chains tended to have more structuring potential per gram of material than shorter chains. Further investigation of how these subtle variations in the amounts and chain length of structurants influence the structural properties of structured oil systems seems of interest, especially if combined with surfactants of different molecular structure, for example, monodiglyceride and polyglycerol polyricinoleate – a classical combination, for low fat water in oil emulsions. Indeed, explanation of these mechanisms is still required (Awad & Sato, 2002; Sakamoto *et al.*, 2003). Sakamoto *et al.* (2003) reported that polyglycerol behenic esters promoted nucleation, but inhibited crystal growth of palm oil and promoted the β' polymorph. Arima *et al.* (2007) reported that stabilisation and retardation effects allowed heterogeneous crystallisation (figure 4) and prohibition of morphological change, because of adsorption at the interfacial membrane. This is a mechanism proposed for templating nucleation (figure 5) and is interesting for low saturated fat systems, where an aqueous phase is included. It is possible that this approach could be useful for nucleation events within organogels, where Duffy *et al.* (2009) and Pernetti *et al.* (2007) suggest mixed systems that employ surfactants, and could offer advantages for structuring of oil continuous emulsions (and in specific cases water continuous emulsions), as many food products are emulsions.

It would be useful to know how alternative "host surfactants" might work with other surfactant combinations (Fujiwara *et al.*, 2000; Sakamoto *et al.*, 2003, 2004). The presence of interfaces, as in emulsions, will influence the creation of building blocks as required for oil structuring. Ishizuka *et al.* (2009) reported that surfactant molecules in water and other solvents can form various self-assembled structures such as micelles and liquid crystals, due to their hydrophobic interaction. The authors found micellar shapes could form varied spherical, to worm-like structures, depending on composition, temperature and other factors. These micelle formations grow to form aggregates and behave like polymers, becoming highly viscoelastic and can entangle each other (Duffy *et al.*, 2009). Therefore, translating these structuring options to emulsions will likely necessitate reformulation. This suggests that rather than focus purely on single components, or perhaps mixed bulk organogel systems, investigation into real systems where aqueous phases are employed could provide useful information (Pernetti *et al.*, 2007; Tanaka *et al.*, 2009).

In the case of a given interfacial emulsifier concentration, temperature, and shear rate, the surface of water droplets will be optimally or sub-optimally covered, especially in the context of HIPREs. Explaining these mechanisms could be problematic, in that laboratory scale techniques using standard methods could be limited because of their inability to provide data whilst under true dynamic conditions. During isothermal conditions, the mechanical orientation of TAG and non-TAG structures and stabilisation could be critical, especially where, for example, TAG structures in themselves do not exhibit polar behaviour. However, at a certain surfactant concentration, the TAG crystals become more polar in behaviour because the surfactant is adsorbed to the TAG surface which theoretically produces more rigid and uniform structures. Evidence suggests that at certain concentrations and ratios of specific surfactants (template additives), the surface of water droplets is more optimally covered because of faster induction of heterogeneous nucleation to

form molecular aggregates, which act as a template for nucleation. Through use of SR- μ -SAXD microscopic analysis of the lamellar plane directions and structural domains could also be performed which might provide a deeper insight into the emulsion crystallisation mechanics.

Understanding how to measure mechanical viscoelastic properties of structurant interactions, both in model and real-time dynamic measurements, for example, UVP-PD, will be necessary (Pernetti *et al.*, 2007; Povey *et al.*, 2007; Schaink *et al.*, 2007; Young *et al.*, 2008; Arima *et al.*, 2009; Ishizuka *et al.*, 2009; Ojijo *et al.*, 2009; Rogers, 2009; Wassell *et al.*, 2010).

CONCLUSION

This review has looked at several systems considered able to structure low saturated fat-based systems and which in themselves could also have emulsification properties. The presence of interfaces, as in emulsions, will interact with the creation of building blocks as required for oil or fat structuring. Although many food products are essentially emulsions, interest in the structuring of oil-continuous emulsions (and in specific cases water-continuous emulsions) will not be straightforward, especially where some more novel structuring materials are used either wholly or partially to replace traditional structurants.

In attempting to reduce the degree of saturates in food systems, it will be necessary to observe effects on mixed structurants and to analyse this relationship when cosurfactant structures are used and how this may influence interfacial film thickness, strength and flexibility.

Understanding how to measure mechanical viscoelastic properties of structurant interactions both in model and real-time dynamic systems will be necessary to account for diffusion, orientation and self-assembly mechanisms. In the case of exploring how novel structures behave within W/O or O/W emulsions, it will be important to understand how interfacial active emulsifiers will behave at these surfaces to form heterogeneous structures.

Clearly, greater understanding of the role of these factors will require further investigation.

The authors consider that the answers to these problems are most likely to be achieved through three main routes; (1) combining traditional techniques with novel structural technology; (2) developing and validating in-line dynamic measurement techniques; and (3) investigation of emulsion systems, as opposed exclusively to single phase model systems.

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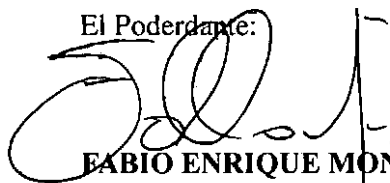
E. S. D.

Yo, **FABIO ENRIQUE MONTENEGRO ESCOBAR**, mayor de edad, vecino de la ciudad de Bogotá, identificado con la Cédula de Ciudadanía No. 3.227.693 de Bogotá, obrando como representante legal de la sociedad domiciliada en Bogotá, que gira bajo la razón social de **C.I. SOCIEDAD INDUSTRIAL DE GRASAS Y VEGETALES S.A. – C.I. SIGRA S.A.**, confiero poder especial, pero amplio y suficiente a **SANTIAGO MÁRQUEZ ROBLEDO**, abogado inscrito ante el Consejo Superior de la Judicatura, identificado con la Cédula de Ciudadanía No. 79.980.922 de Bogotá, portador de la Tarjeta Profesional de Abogado No. 131.853, y/o **JORGE MÁRQUEZ CUERVO**, mayor de edad y vecino de esta ciudad, abogado en ejercicio con T.P. 49.528 del C.S. de la J., identificado con la cédula de ciudadanía No. 17.164.571 de Bogotá, y/o **ANDRES GARCÍA FLÓREZ**, mayor y vecino de esta ciudad, abogado en ejercicio con T.P. 58.586 del C.S. de la J., identificado con la cédula de ciudadanía No. 79.240.773 de Bogotá, para que presente memorial en contra de la solicitud de registro de la patente de invención denominada **PRODUCTO GRASO SOLIDO CON BAJO CONTENIDO DE GRASA SATURADA Y LIBRE DE ACIDOS GRASOS TRANS**, Expediente No. 10-92087, presentada por la sociedad **TEAM FOODS COLOMBIA S.A.**, argumentando la falta de novedad de la misma.

El apoderado queda ampliamente facultado para el cabal cumplimiento del presente poder, así como para recibir, desistir, transigir, conciliar, sustituir y reasumir.

Sírvase reconocerle personería.

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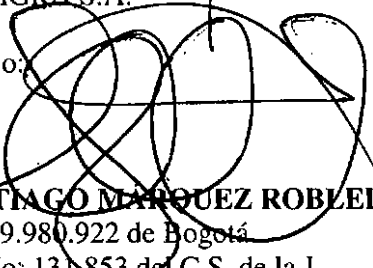
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ANDRES GARCÍA FLÓREZ

C.C. 79.240.773 de Bogotá

T.P. 58.586 del C.S. de la J.



DILIGENCIA DE PRESENTACIÓN
PERSONAL Y RECONOCIMIENTO

CARLOS ALBERTO RAMIREZ PARDO
NOTARIO 48 (E) BOGOTÁ D.C.

Bogotá D.C. 15/11/2011

swwde4s2322wz22

La Suscrita(o) Notaria(o) certifica que este escrito fué presentado
por quien dijo llamarse:

MONTENEGRO ESCOBAR FABIO
Identificado con: C.C. 3227693



quien declaró que su contenido es cierto y que la firma y huella
puestas en él son suyas.

FIRMA:

HUELLA:

[Handwritten signature]





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CAMARA DE COMERCIO DE BOGOTA

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CERTIFICADO DE EXISTENCIA Y REPRESENTACION LEGAL O INSCRIPCION DE DOCUMENTOS

LA CAMARA DE COMERCIO DE BOGOTA, CON FUNDAMENTO EN LAS MATRICULAS E INSCRIPCIONES DEL REGISTRO MERCANTIL

CERTIFICA:

NOMBRE : C I SOCIEDAD INDUSTRIAL DE GRASAS VEGETALES SIGRA S A Y PODRA UTILIZAR LA SIGLA C I SIGRA S A

SIGLA : C I SIGRA S A

N.I.T. : 860006127-4

DOMICILIO : BOGOTA D.C.

CERTIFICA:

MATRICULA NO: 00012756 DEL 29 DE MARZO DE 1972

CERTIFICA:

DIRECCION DE NOTIFICACION JUDICIAL : CR 46 13 95

MUNICIPIO : BOGOTA D.C.

EMAIL DE NOTIFICACION JUDICIAL : belsi.contreras@sgra.com

DIRECCION COMERCIAL : CR 46 13 95

MUNICIPIO : BOGOTA D.C.

EMAIL COMERCIAL : belsi.contreras@sgra.com

CERTIFICA:

CONSTITUCION: ESCRITURA PUBLICA NO.1648, NOTARIA 5 DE BOGOTA, EL-6 DE ABRIL DE 1.957, INSCRITA EL 9 DE ABRIL DE 1.957, BAJO EL NO. 36.932 DEL LIBRO RESPECTIVO, SE CONSTITUYO LA SOCIEDAD DENOMINADA SOCIEDAD INDUSTRIAL LIMITADA DE GRASAS VEGETALES SIGRA.

CERTIFICA:

QUE POR ESCRITURA PUBLICA NO. 295, NOTARIA 32 DE BOGOTA EL 9 DE MAYO DE 1.982, INSCRITA EN ESTA CAMARA DE COMERCIO EL 12 DE MAYO DE 1982, BAJO EL NO. 115.653 DEL LIBRO IX, LA SOCIEDAD ADICIONO A SU RAZON SOCIAL LA SIGLA SIGRA S.A. E INTRODUJO OTRAS REFORMAS.

CERTIFICA :

QUE POR ESCRITURA PUBLICA NO. 1303 DEL 07 DE JUNIO DE 2004 DE LA NOTARIA 52 DE BOGOTA D.C., INSCRITA EL 25 DE JUNIO DE 2004 BAJO EL NUMERO 00940588 DEL LIBRO IX, LA SOCIEDAD CAMBIO SU NOMBRE DE: SOCIEDAD INDUSTRIAL DE GRASAS VEGETALES SIGRA S.A., POR EL DE: SOCIEDAD INDUSTRIAL DE GRASAS VEGETALES SIGRA S. A. Y PODRA UTILIZAR LA SIGLA SIGRA S.A.-

CERTIFICA :

QUE POR ESCRITURA PUBLICA NO. 2581 DE LA NOTARIA 52 DE BOGOTA D.C. DEL 28 DE OCTUBRE DE 2004, INSCRITA EL 02 DE NOVIEMBRE DE 2004 BAJO EL NUMERO 960096 DEL LIBRO IX, LA SOCIEDAD DE LA REFERENCIA CAMBIO SU NOMBRE DE: SOCIEDAD INDUSTRIAL DE GRASAS VEGETALES SIGRA S. A. Y PODRA UTILIZAR LA SIGLA SIGRA S.A. , POR EL DE : C.I. SOCIEDAD INDUSTRIAL DE GRASAS VEGETALES SIGRA S.A. Y PODRA UTILIZARLA SIGLA C.I. SIGRA S.A.

CERTIFICA:

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QUE POR ESCRITURA PUBLICA NO. 7179, NOTARIA 5 DE BOGOTA EL 28 DE OCTUBRE DE 1.961, INSCRITA EN ESTA CAMARA DE COMERCIO EL 16 DE NOVIEMBRE DE 1.961, BAJO EL NO. 30.109 DEL LIBRO RESPECTIVO, LA SOCIEDAD SE TRANSFORMO DE LIMITADA EN ANONIMA BAJO EL NOMBRE DE SOCIEDAD INDUSTRIAL DE GRASAS VEGETALES SIGRA S.A.

CERTIFICA:

REFORMAS:

ESCRITURAS NO.	FECHA	NOTARIA	INSCRIPCION
6750	10-XII -1957	5 BOGOTA	38.831-18-XII -1957
1408	20-III -1958	5 BOGOTA	39.691- 1-IV -1958
1411	20-III -1958	5 BOGOTA	39.747- 8-IV -1958
3942	7-VII -1958	5 BOGOTA	40.530-16-VII -1958
845	19-II -1959	5 BOGOTA	42.431-26-II -1959
1713	2-IX -1959	5 BOGOTA	42.801-10-IV -1959
6424	24-IX -1959	5 BOGOTA	44.364-29-IX -1959
4080	7-VII -1960	5 BOGOTA	46.933-13-VII -1960
6244	10-X -1960	5 BOGOTA	47.829-20-X -1960
8016	20-XII -1960	5 BOGOTA	48.440-23-XII -1960
6399	30-IX -1961	5 BOGOTA	51.233- 7-X -1961
6666	10-X -1961	5 BOGOTA	51.314-17-X -1961
1446	12-III -1963	5 BOGOTA	51.516-14-III -1963
690	28-II -1972	4 BOGOTA	4.575- 5-IX -1972
2322	19-VI -1989	7 BOGOTA	274.910-14-IX -1989
1640	22-IV- 1990	7 BOGOTA	293.475- 8-V- 1990
2321	25 -V- 1992	7 STAFE BTA	367.825- 9-VI- 1992
5529	3-XI- 1993	7 STAFE BTA	427.139- 12-XI -1993
3176	13-VII-1995	7 STAFE BTA	502.208- 27-VII-1995
787	6- III-1996	7 STAFE BTA	531.544 20- III-1996

CERTIFICA:

REFORMAS:

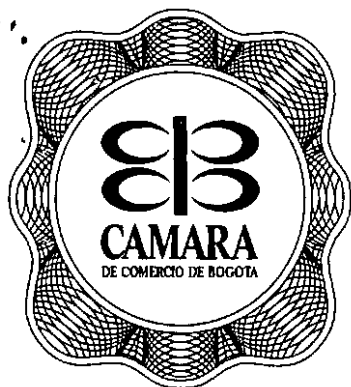
E.P. NO.	FECHA	NOTARIA	CIUDAD	FECHA	NO. INSC.
0001303	2004/06/07	0052	BOGOTA D.C.	2004/06/25	00940588
0002581	2004/10/29	0052	BOGOTA D.C.	2004/11/02	00960096
0001071	2006/04/27	0052	BOGOTA D.C.	2006/08/03	01070557
0001683	2007/08/13	0052	BOGOTA D.C.	2007/09/03	01155313
2684	2009/10/13	0052	BOGOTA D.C.	2009/12/22	01349429
1998	2010/10/21	0050	BOGOTA D.C.	2010/10/25	01423895
1212	2011/05/30	0050	BOGOTA D.C.	2011/06/09	01486431

CERTIFICA:

VIGENCIA: QUE LA SOCIEDAD NO SE HALLA DISUELTA. DURACION HASTA EL 31 DE DICIEMBRE DE 2030 .

CERTIFICA:

OBJETO SOCIAL: LA SOCIEDAD TIENE POR OBJETO SOCIAL PRINCIPAL EL DESARROLLO DE LAS SIGUIENTES ACTIVIDADES: 1. EFECTUAR OPERACIONES DE COMERCIO EXTERIOR Y PARTICULARMENTE ORIENTAR SUS ACTIVIDADES HACIA LA PROMOCIÓN, COMERCIALIZACIÓN Y VENTA DE LOS PRODUCTOS COLOMBIANOS EN LOS MERCADOS EXTERNOS; 2. LA ELABORACIÓN, COMERCIALIZACIÓN, DISTRIBUCIÓN Y EXPORTACIÓN DE PRODUCTOS GRASOS FABRICADOS A PARTIR DEL PROCESAMIENTO DE GRASAS Y ACEITES DE ORIGEN VEGETAL, ANIMAL Y/O UNA MEZCLA DE ELLOS; 3. LA PRODUCCIÓN, DISTRIBUCIÓN Y EXPORTACIÓN DE MATERIAS PRIMAS DE DIVERSAS CLASES QUE SE EMPLEEN EN LA ELABORACIÓN DE PRODUCTOS GRASOS, ASÍ COMO LAS DE LOS IMPLEMENTOS, MAQUINARIAS, EQUIPOS MUEBLES Y DEMÁS ELEMENTOS QUE SE UTILICEN O PUEDAN UTILIZARSE PARA LA ELABORACIÓN, COMERCIALIZACIÓN Y DISTRIBUCIÓN DE DICHOS PRODUCTOS GRASOS O DE LOS SUBPRODUCTOS ELABORADOS PARA ESTE FIN Y PARA LA TRANSFORMACIÓN Y DISTRIBUCIÓN DE LOS SUBPRODUCTOS RESULTANTES DE



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ESTOS PROCESOS; 4. LA VENTA, COMERCIALIZACIÓN, DISTRIBUCIÓN, IMPORTACIÓN, EXPORTACIÓN Y VENTA DE LOS BIENES PRODUCIDOS O TRANSFORMADOS POR ELLA DIRECTAMENTE, POR CUENTA DE TERCEROS Y/O PARTICIPACIÓN EN LOS MISMOS, SIEMPRE QUE AQUELLOS, TENGAN RELACIÓN DIRECTA CON EL OBJETO SOCIAL ANTES MENCIONADO. 5. LA CONSTITUCIÓN DE SOCIEDADES COMERCIALES E INDUSTRIALES EN EL TERRITORIO NACIONAL O EN EL EXTERIOR Y LA PARTICIPACIÓN EN ESTAS COMO SOCIA O ACCIONISTA. 6. LA IMPORTACIÓN DE BIENES O INSUMOS CON LA FINALIDAD DE ABASTECER EL MERCADO INTERNO O PARA LA FABRICACIÓN DE PRODUCTOS EXPORTABLES; 7. LA IMPLEMENTACIÓN Y DESARROLLO DE CUALQUIER ACTIVIDAD AGRÍCOLA COMO EL CULTIVO DE PRODUCTOS DE CORTO Y TARDÍO RENDIMIENTO, ASÍ COMO EL CULTIVO DE ÁRBOLES MADERABLES, ENTRE OTROS. DENTRO DE LOS PRODUCTOS QUE LA SOCIEDAD PUEDE CULTIVAR SE ENCUENTRA LA PALMA AFRICANA, EL CAUCHO Y EL CACAO, ENTRE OTROS; 8. LA IMPLEMENTACIÓN Y DESARROLLO DE TODO TIPO DE ACTIVIDADES PECUARIAS SIN LIMITACIÓN, TALES COMO LA CRÍA, LEVANTE Y CEBA DE GANADO, ENTRE OTROS. PARA EL CUMPLIMIENTO DE SU OBJETO SOCIAL PRINCIPAL, LA SOCIEDAD PODRÁ: 1. REPRESENTAR A CUALQUIER COMPAÑÍA NACIONAL O EXTRANJERA PARA EFECTOS DE COMERCIALIZAR, DISTRIBUIR Y ELABORAR CUALQUIER CLASE DE PRODUCTOS RELACIONADOS CON EL OBJETO SOCIAL ANTERIOR 2. ADQUIRIR, ARRENDAR, ADMINISTRAR, GRAVAR, PRESTAR Y ENAJENAR BIENES MUEBLES E INMUEBLES; DARLOS EN ADMINISTRACIÓN O TOMARLOS EN ARRIENDO. 3. ADQUIRIR, POSEER, DAR O TOMAR EN ARRENDAMIENTO O A OTRO TÍTULO ONEROSO Y ENAJENAR, EQUIPOS, INSTALACIONES, MAQUINARIA INDUSTRIAL, MUEBLES U OTROS IMPLEMENTOS O ACTIVOS DESTINADOS A LA DOTACIÓN, FUNCIONAMIENTO Y EXPLOTACIÓN DE EMPRESAS INDUSTRIALES, COMERCIALES O DE SERVICIOS. 4. FORMAR PARTE DE OTRAS SOCIEDADES CUALQUIERA QUE SEA SU NATURALEZA Y OBJETO SOCIAL, ADQUIRIENDO O SUSCRIBIENDO ACCIONES, PARTES O CUOTAS DE INTERÉS SOCIAL O HACIENDO APORTES DE CUALQUIER ESPECIA O FUSIONARSE CON OTRAS SOCIEDADES 5. ADQUIRIR, POSEER, Y EXPLOTAR PATENTES, NOMBRES COMERCIALES, MARCAS, SECRETOS INDUSTRIALES, LICENCIAS U OTROS DERECHOS CONSTITUTIVOS DE PROPIEDAD INDUSTRIAL; LA CONCESIÓN DE SU EXPLOTACIÓN A TERCEROS, ASÍ COMO LA ADQUISICIÓN DE CONCESIONES PARA SU EXPLOTACIÓN. 6. INVERTIR EN BIENES MUEBLES E INMUEBLES EFECTUAR SU NEGOCIACIÓN, VENTA PERMUTA, GRAVAMEN, ETC, PUDIENDO RESPECTO DE LOS INMUEBLES, PROMOVER O EJECUTAR TODOS LOS NEGOCIOS RELACIONADOS CON FINCA RAÍZ, 7. EFECTUAR OPERACIONES DE CRÉDITO RELACIONADAS CON LA ADQUISICIÓN O VENTA DE BIENES MUEBLES O INMUEBLES. 8. CELEBRAR CONTRATOS DE MUTUO, CON O SIN INTERESES. 9. CONSTITUIR CAUCIONES REALES O PERSONALES EN GARANTÍA DE LAS OBLIGACIONES QUE CONTRAIGA LA SOCIEDAD, O SOCIEDADES O EMPRESAS EN LAS QUE TENGA INTERÉS, SIEMPRE QUE, EN EL ÚLTIMO CASO SE CUENTE CON LA PREVIA APROBACIÓN DE LA JUNTA DIRECTIVA. 10. INVERTIR SUS FONDOS O DISPONIBILIDADES, EN ACTIVOS FINANCIEROS O VALORES MOBILIARIOS TALES COMO TÍTULOS EMITIDOS POR INSTITUCIONES FINANCIERAS O ENTIDADES PÚBLICAS, CÉDULAS HIPOTECARIAS,

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TÍTULOS VALORES, BONOS, ENTRE OTROS, ASÍ COMO SU NEGOCIACIÓN, VENTA, PERMUTA O GRAVAMEN. 11. COMPRAR Y VENDER, IMPORTAR Y EXPORTAR. CUALQUIER CLASE DE BIENES, ARTÍCULOS O MERCADERÍAS RELACIONADAS CON LOS NEGOCIOS PRINCIPALES, QUE FACILITEN EL CUMPLIMIENTO DEL OBJETO SOCIAL. 12. PARTICIPAR EN LICITACIONES Y CONCURSOS PÚBLICOS Y PRIVADOS O EN CONTRATACIONES DIRECTAS. 13. PRESTAR SERVICIOS RELATIVOS A LA COMERCIALIZACIÓN DE PRODUCTOS DERIVADOS DE GRASAS Y ACEITES VEGETALES, ANIMALES Y/O MEZCLAS, MATERIAS PRIMAS DE DIVERSAS CLASES QUE SE EMPLEEN EN LA ELABORACIÓN DE TALES GRASAS Y ACEITES, ASÍ COMO LOS DEMÁS IMPLEMENTOS Y ELEMENTOS QUE SE UTILICEN O PUEDAN UTILIZARSE PARA LA PRODUCCIÓN, TRANSFORMACIÓN, DISTRIBUCIÓN Y COMERCIALIZACIÓN DE LOS MENCIONADOS PRODUCTOS. 14. EN GENERAL, EJECUTAR, DESARROLLAR Y LLEVAR A TÉRMINO TODOS AQUELLOS ACTOS O CONTRATOS RELACIONADOS DIRECTAMENTE CON LOS QUE CONSTITUYAN SU OBJETO SOCIAL.

CERTIFICA:

CAPITAL:

** CAPITAL AUTORIZADO **

VALOR : \$2,600,000,000.00
NO. DE ACCIONES : 2,600,000,000.00
VALOR NOMINAL : \$1.00

** CAPITAL SUSCRITO **

VALOR : \$1,536,380,220.00
NO. DE ACCIONES : 1,536,380,220.00
VALOR NOMINAL : \$1.00

** CAPITAL PAGADO **

VALOR : \$1,536,380,220.00
NO. DE ACCIONES : 1,536,380,220.00
VALOR NOMINAL : \$1.00

CERTIFICA:

** JUNTA DIRECTIVA: PRINCIPAL (ES) **

QUE POR ACTA NO. 91 DE ASAMBLEA DE ACCIONISTAS DEL 25 DE JULIO DE 2011, INSCRITA EL 25 DE JULIO DE 2011 BAJO EL NUMERO 01498172 DEL LIBRO IX, FUE (RON) NOMBRADO (S):

NOMBRE	IDENTIFICACION
PRIMER RENGLON	
ROZO RUBIANO BERNARDO	C.C. 000000000437813
SEGUNDO RENGLON	
MOTTA VENEGAS LUIS ALFREDO	C.C. 000000019128214
TERCER RENGLON	
RIBON CATALA MIGUEL GERMAN	C.C. 000000003229310
CUARTO RENGLON	
STASIUKYNAS ADOMAITIS DIANA REGINA	C.C. 000000035473295
QUINTO RENGLON	
NOVOA ROJAS FABIO	C.C. 000000019183720

** JUNTA DIRECTIVA: SUPLENTE (S) **

QUE POR ACTA NO. 91 DE ASAMBLEA DE ACCIONISTAS DEL 25 DE JULIO DE 2011, INSCRITA EL 25 DE JULIO DE 2011 BAJO EL NUMERO 01498172 DEL LIBRO IX, FUE (RON) NOMBRADO (S):

NOMBRE	IDENTIFICACION
PRIMER RENGLON	
MONTENEGRO ESCOVAR CARLOS HERNANDO	C.C. 000000019439284
SEGUNDO RENGLON	
MONTENEGRO ESCOVAR ANGELA PATRICIA	C.C. 000000035506790
TERCER RENGLON	



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MONTENEGRO JUAN FELIPE C.C.. 000001020728452
CUARTO RENGLON
MONTENEGRO ESCOBAR OLGA MARIA DEL PILAR C.C. 000000041714941
QUINTO RENGLON
MONTENEGRO ESCOBAR JORGE ALBERTO C.C. 000000019210081

CERTIFICA:

REPRESENTACION LEGAL: LA SOCIEDAD TENDRA UN GERENTE GENERAL, ASI COMO UN SUPLENTE QUE LO REEMPLAZARA EN SUS FALTAS ACCIDENTALES Y TEMPORALES. EL GERENTE O QUIEN HAGA SUS VECES SERA EL REPRESENTANTE LEGAL PRINCIPAL DE LA SOCIEDAD PARA TODOS LOS EFECTOS.-

CERTIFICA:

** NOMBRAMIENTOS **

QUE POR ACTA NO. 0000576 DE JUNTA DIRECTIVA DEL 15 DE JUNIO DE 2004, INSCRITA EL 25 DE JUNIO DE 2004 BAJO EL NUMERO 00940589 DEL LIBRO IX, FUE (RON) NOMBRADO (S):

NOMBRE	IDENTIFICACION
GERENTE	
MONTENEGRO ESCOBAR FABIO ENRIQUE	C.C. 000000003227693
SUPLENTE DEL GERENTE	
MONTENEGRO ESCOBAR JORGE ALBERTO	C.C. 000000019210081

CERTIFICA:

FACULTADES DEL REPRESENTANTE LEGAL: SON FUNCIONES ESPECIALES DEL GERENTE GENERAL : REPRESENTAR A LA SOCIEDAD COMO PERSONA JURIDICA. PARTICIPAR CON VOZ PEROS SIN VOTO EN LA JUNTA DIRECTIVA Y RENDIR CUENTAS DE SU GESTION. EJECUTAR Y HACER EJECUTAR LOS ACUERDOS Y RESOLUCIONES DE LA ASAMBLEA GENERAL DE ACCIONISTAS Y DE LA JUNTA DIRECTIVA. CUMPLIR LAS ORDENES E INSTRUCCIONES QUE LE IMPARTA LA JUNTA DIRECTIVA, Y SOLICITAR AUTORIZACION PARA LOS NEGOCIOS QUE DEBA APROBAR PREVIAMENTE LA JUNTA DIRECTIVA, CONFORME A LOS PRESENTES ESTATUTOS. CON LAS RESTRICCIONES QUE ESTABLECEN LA LEY Y LOS ESTATUTOS, EL GERENTE GENERAL PODRA CELEBRAR O EJECUTAR TODOS LOS ACTOS Y CONTRATOS COMPRENDIDOS DENTRO DEL OBJETO SOCIAL O QUE SE RELACIONEN DIRECTAMENTE CON LA EXISTENCIA Y EL FUNCIONAMIENTO DE LA SOCIEDAD. NOMBRAR Y REMOVER LIBREMENTE TODOS LOS EMPLEADOS DE LA SOCIEDAD, CUYO NOMBRAMIENTO NO ESTE ATRIBUIDO A LA ASAMBLEA GENERAL NI A LA JUNTA DIRECTIVA. TOMAR TODAS LAS MEDIDAS QUE RECLAME LA CONSERVACION DE LOS BIENES SOCIALES, VIGILAR LA ACTIVIDAD DE LOS EMPLEADOS DE LA ADMINISTRACION E IMPARTIRLES LAS ORDENES E INSTRUCCIONES QUE EXIJA LA BUENA MARCHA DE LA COMPAÑIA. PRESENTAR OPORTUNAMENTE, A LA CONSIDERACION DE LA JUNTA DIRECTIVA, EL PRESUPUESTO DE INVERSIONES, INGRESOS Y GASTOS QUE REQUIERE LA COMPAÑIA. PRESENTAR A LA SOLICITUD DE LA JUNTA DIRECTIVA LOS ESTADOS FINANCIEROS DE PROPOSITO GENERAL INDIVIDUALES, Y CONSOLIDADOS

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CUANDO SEA DEL CASO, CON SUS NOTAS, CORTADOS AL FIN DEL RESPECTIVO EJERCICIO, JUNTO CON LOS DOCUMENTOS QUE SEÑALE LA LEY Y EL INFORME DE GESTION, ASI COMO EL ESPECIAL CUANDO SE DE LA CONFIGURACION DE UN GRUPO EMPRESARIAL, TODO LO CUAL SE PRESENTARA A LA ASAMBLEA GENERAL DE ACCIONISTAS. AL IGUAL QUE LOS DEMAS ADMINISTRADORES, DEBERA RENDIR CUENTAS COMPROBADAS DE SU GESTION AL FINAL DE CADA EJERCICIO, DENTRO DEL MES SIGUIENTE A LA FECHA EN EL CUAL SE RETIRE DE SUS CARGO Y CUANDO SE LAS EXIJA EL ORGANO QUE SEA COMPETENTE PARA ELLO. PARA TAL EFECTO, SE PRESENTARAN LOS ESTADOS FINANCIEROS QUE FUEREN PERTINENTES, JUNTO CON UN INFORME DE GESTION. CUMPLIR LOS DEMAS DEBERES QUE LE SEÑALEN LOS REGLAMENTOS DE LA SOCIEDAD Y LOS QUE LE CORRESPONDEN POR EL CARGO QUE EJERCE. PARAGRAFO : EN TODO CASO EL GERENTE GENERAL TENDRA ATRIBUCIONES SUFICIENTES PARA ORDENAR QUE SE EJECUTE O CELEBRE CUALQUIER ACTO O NEGOCIO COMPRENDIDO DENTRO DEL OBJETO SOCIAL Y PARA TOMAR LAS DETERMINACIONES NECESARIAS EN ORDEN A QUE LA SOCIEDAD CUMPLA SUS FINES, CUANDO LA CUANTIA NO EXCEDA DE UN MIL (1000) SALARIOS MINIMOS LEGALES MENSUALES. EN CASO DE QUE SE REQUIERA SOBREPASAR DICHA CUANTIA, LA AUTORIZACION DEBERA SER DADA POR LA JUNTADIRECTIVA.-

CERTIFICA:

** REVISOR FISCAL **

QUE POR DOCUMENTO PRIVADO DE REVISOR FISCAL DEL 30 DE MARZO DE 2011, INSCRITA EL 9 DE JUNIO DE 2011 BAJO EL NUMERO 01486435 DEL LIBRO IX, FUE (RON) NOMBRADO (S):

NOMBRE	IDENTIFICACION
REVISOR FISCAL PRINCIPAL	
RUBIO TELLEZ LUIS ENRIQUE	C.C. 000000019189135
REVISOR FISCAL SUPLENTE	
SAMACA SANCHEZ LIGIA INES	C.C. 000000020320002

QUE POR ACTA NO. 91 DE ASAMBLEA DE ACCIONISTAS DEL 30 DE MARZO DE 2011, INSCRITA EL 9 DE JUNIO DE 2011 BAJO EL NUMERO 01486423 DEL LIBRO IX, FUE (RON) NOMBRADO (S):

NOMBRE	IDENTIFICACION
REVISOR FISCAL PERSONA JURIDICA	
RUBIO SAMACA Y CIA LTDA	N.I.T. 000008000848538

CERTIFICA:

PERMISO DE FUNCIONAMIENTO: QUE POR RESOLUCION NO.0062 DEL 25 DE - ENERO DE 1.962, INSCRITA EL 26 DE ENERO DE 1.962, BAJO EL NUMERO 30301 DEL LIBRO RESPECTIVO, LA SUPERINTENDENCIA DE SOCIEDADES OTORGO PERMISO DEFINITIVO DE FUNCIONAMIENTO.-----

CERTIFICA:

QUE LA SOCIEDAD TIENE MATRICULADOS LOS SIGUIENTES ESTABLECIMIENTOS:

NOMBRE : SOCIEDAD INDUSTRIAL DE GRASAS VEGETALES SIGRA

MATRICULA NO : 00073805 DE 30 DE ABRIL DE 1976

RENOVACION DE LA MATRICULA : EL 25 DE MARZO DE 2011

ULTIMO AÑO RENOVADO : 2011

NOMBRE : COGRA INDUSTRIAL PANADERIA

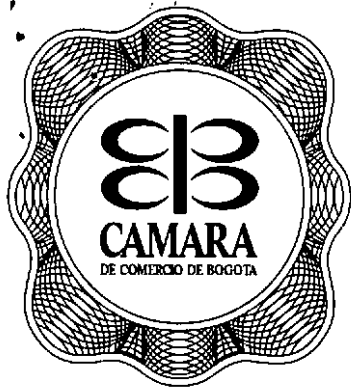
MATRICULA NO : 01179270 DE 3 DE MAYO DE 2002

RENOVACION DE LA MATRICULA : EL 25 DE MARZO DE 2011

ULTIMO AÑO RENOVADO : 2011

CERTIFICA:

DE CONFORMIDAD CON LO ESTABLECIDO POR LA LEY 962 DE 2005, LOS ACTOS DE REGISTRO AQUI CERTIFICADOS QUEDAN EN FIRME CINCO (5) DIAS HABILES



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DESPUES DE LA FECHA DE INSCRIPCION, SIEMPRE QUE NO SEAN OBJETO DE RECURSOS EN LA VIA GUBERNATIVA.

* * * EL PRESENTE CERTIFICADO NO CONSTITUYE PERMISO DE * * *
 * * * FUNCIONAMIENTO EN NINGUN CASO * * *

SEÑOR EMPRESARIO, SI SU EMPRESA TIENE ACTIVOS INFERIORES A 30.000 SMLMV Y UNA PLANTA DE PERSONAL DE MENOS DE 200 TRABAJADORES, USTED TIENE DERECHO A RECIBIR UN DESCUENTO EN EL PAGO DE LOS PARAFISCALES DE 75% EN EL PRIMER AÑO DE CONSTITUCION DE SU EMPRESA, DE 50% EN EL SEGUNDO AÑO Y DE 25% EN EL TERCER AÑO. LEY 590 DE 2000 Y DECRETO 525 DE 2009.

RECUERDE INGRESAR A www.supersociedades.gov.co PARA VERIFICAR SI SU EMPRESA ESTA OBLIGADA A REMITIR ESTADOS FINANCIEROS. EVITE SANCIONES.

EL SECRETARIO DE LA CAMARA DE COMERCIO,
 VALOR : \$ 3,700

DE CONFORMIDAD CON EL DECRETO 2150 DE 1995 Y LA AUTORIZACION IMPARTIDA POR LA SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO, MEDIANTE EL OFICIO DEL 18 DE NOVIEMBRE DE 1996, LA FIRMA MECANICA QUE APARECE A CONTINUACION TIENE PLENA VALIDEZ PARA TODOS LOS EFECTOS LEGALES