

AFTERNOON

EAT 1: Functional Lipids

Chair(s): D. Nakhasi, Bunge Oils Inc., USA; and F. Orthoefer, FTO Food Research, USA

Structuring Oils for Use in Shortening System with Reduced Saturated Fatty Acids without Impacting the Functionality - Saturate Sparing Shortening System. D. Nakhasi, N. Higgins, Bunge North America, Inc, Bradley, IL, USA

Utilization of proprietary non-lipid ingredients, blending and crystallization processes (triglyceride mismatch) provides the capability to reduce all purpose and emulsified shortenings saturate levels by greater than 40%. The technology is based on two separate but contributing inventions. A unique hard stock blend, plus a fiber addition, once combined enable the shortening system to trap and bind large amounts of free oil, while still contributing structure. The concept was to develop a functional plastic shortening with reduced levels of saturated fatty acids by utilization of cellulose fibers and triglyceride mis-match technology. This technology successfully provides us the means to achieve the functional shortenings with saturates at 17 -19%. Nutritional analysis indicates that it is virtually trans free with 40% reduced saturated fatty acid when compared to conventional reduced trans shortenings. Applications results have revealed that saturate sparing shortening can be used in many all purpose and emulsified shortening applications. It can be utilized in place of other all purposes shortenings, to confer the nutritional benefits of reduced saturates without affecting the taste or mouth feel of the finished product.

Impact of Alpha Linolenic Acid (ALA) Levels and TBHQ on Low Saturate High Oleic Soybean Oil Performance. R. Wilkes, L. Jurado, Monsanto Company, St. Louis, MO USA

Low saturated fat high oleic soybean oil has been developed that enables food companies and food service operators to provide their customers with foods having reduced saturated fat, low trans fat, and longer shelf life. Use of this oil meets the 2010 Dietary Guidelines to reduce the use of solid fats including *trans* and saturated fat and replace them with liquid oils high in monounsaturated and polyunsaturated fat. Past fry studies have demonstrated excellent fry performance and sensory acceptability. In the current study, the impact of TBHQ and varying levels of alpha linolenic acid were evaluated both from a fry performance and storage study using tortilla chips fried in the new oil. Analytical, fry performance and sensory results will be presented. Additionally, results of a dietary intake modeling study will be presented that demonstrates the potential to reduce saturated fat intake for quick service restaurant (QSR) customers when this oil is substituted for oil blends currently being used.

Novel Applications of Omega-3 Fatty Acids in Foods, Supplements and Pharma. E. Hernandez, Omega Protein Inc., Houston, TX, USA

The role of Omega-3 fatty acids, eicosapentaenoic (EPA) and docosahexaenoic (DHA), in nutrition and disease prevention has been widely documented in numerous research studies and clinical trials. This is reflected by the accelerated growth of omega-3 fats applications in the food, supplement and pharmaceutical markets, which has grown in the US to over \$5 billion. EPA is generally associated with cardiovascular protection; it has been reported to have strong anti-inflammatory, anti-thrombotic, anti-arrhythmic and anti-atherogenic effects. DHA is generally related to cell structures, and has been found to be particularly important in neurologically related metabolism such brain and retina development and function. Omega-3s have been approved for treatment of high blood triglycerides and are actively being investigated of as therapeutic agents in several inflammatory related diseases such as arthritis,

inflammatory bowel disease and some cancers. This presentation will include a review of methods of preparation of new Omega-3 products recently introduced in the market such as omega-3 ethyl esters concentrates of DHA and EPA, structured triglycerides and phospholipids for food, supplements and pharma applications. It also will include a review of new delivery systems in the form of nano dispersions, nano encapsulates and water soluble products.

Specialty Canola Oil Containing 80% Oleic Acid and its Functionality in Food Formulation. Diliara Iassonova, Lorin DeBonte, Linsen Liu, Cargill Incorporated, Fort Collins, CO, USA

High stability oil is essential to maintain desired food flavors for shelf stable food products such as snacks and bake mix. This presentation introduces the first commercially available high oleic canola oil with 80% oleic acid, which deliver the highest stability among plant oils without hydrogenation and trans fat. Its potential applications to increase shelf life and reduce packaging cost are demonstrated.

Physicochemical Properties of Fats for Puff Pastry Formulated with Blends of Soybean Oil and Interesterified Soybean Fats Using a Neural Network. B. Mattioni¹, K. Gandra², D. Barrera-Arellano², J.M. Block¹, ¹Santa Catarina Federal University, Florianopolis, Santa Catarina, Brazil, ²Campinas State University, Campinas, Sao Paulo, Brazil

The main performance characteristics of puff pastry fats include its Solid Fat Content (SFC) and melting properties. In this work a multilayer perceptron neural artificial network was applied in the formulation of zero *trans* fats for puff pastry. The fats were formulated with blends of soybean oil and two interesterified soybean fats. The neural network input was the solid fat content and the melting point of a commercial fat for puff pastry used as the standard fat. Three different formulations were selected and the SFC, melting point (MP), crystallization rate under static conditions, fatty acids profile and triacylglycerol profile were determined. The results showed that the physicochemical properties were very similar to the samples predicted by the neural network and experimentally determined. The results provided by the neural network showed lower SFC, MP, induction time of crystallization and trisaturated triacylglycerols content in comparison with the standard fat. Although softer than the commercial fat the formulations proposed by the neural network showed a relatively high SFC and a wide plasticity range, characteristics that ensure good baking properties for this kind of fat.

Use of Saturated Diglycerides as Additives for Minimizing Oil Migration - Methodology, Modeling, and Results. J. Botts, J. Robertson, Caravan Ingredients, Lenexa, KS, USA

A technique to monitor oil migration of a Nile red labeled stearic-based fat through a lauric-based fat matrix was developed. The sample matrices were incubated at 66°F and 80 °F and imaged at select time intervals. A MatLab[®] algorithm was developed to analyze the images. The algorithm compared the color space of each pixel against the baseline color space to determine the total dyed area. The oil migration rate was mathematically modeled using Fick's second law for isotropic diffusion in two dimensions. The modeled results were then applied to project the diffusion process through the thickness of the sample. The results of the optical method were used to develop a thermokinetic technique utilizing a thermal activity monitor to observe the heat signature associated with the diffusion process. Analysis of the heat signal provides a secondary method to calculate the diffusion coefficient, which appears to correlate to differences in the crystal network. Understanding the nature of the crystalline network allows for identification of additives that can potentially decrease the rate of oil migration, thereby improving the shelf life of finished applications. The thermokinetic method can be applied to systems of indefinite complexity.

High Oleic Canola Oils and their Food Applications. Lorin DeBonte, Diliara Iassonova, Linsen Liu, Cargill, Incorporated, Fort Collins, CO, USA

High oleic and low linolenic canola oils are the major healthy oils in replacement of trans fat in many food applications. Through breeding, linolenic and linoleic acids can be reduced to minimize their negative impact on oil stability. In some food applications such as frying, linoleic acid contributes preferred flavor profile and therefore need be maintained at desired level. In most shelf stable food applications, however, linoleic acid may develop rancidity over time and therefore shorten shelf life of commercial products. To achieve shelf life required by supply chain using

ingredient oil high in linoleic acid, costly packaging and nitrogen flushing have to be used to maintain flavor stability. Cargill Incorporated recently developed and commercialized Clear Valley 80 high oleic canola oil (CV80) through breeding. This new high oleic canola oil, containing at least 80% oleic acid, is the most stable oil among natural and commercial vegetable oils. Its super high stability can improve and enable many new applications such as improving food flavor stability, maintain preferred flavors over transportation and storage, extend shelf life, and reduce packaging cost.

Changing the Microstructure of a High Saturated Shortening using Power Ultrasound. Y. Ye, S. Martini, Utah State University, Logan, UT, USA

Alternative lipid sources and novel processing conditions are being sought to improve the nutritional and functional properties of shortenings. Previous research in our laboratory has shown that power ultrasound can be used as a novel processing technology to improve the physicochemical properties of functional lipids, such as zero-trans and low saturated fats. The objective of our research is to use power ultrasound to change the microstructure of a zero-trans, high saturated shortening with the ultimate goal of obtaining a softer material. Results from this research show that the crystallization of shortening was significantly delayed by the power ultrasound with an increase in crystal size as evidenced by the polarized light microscopy. Viscoelastic properties of the material showed that these processing conditions resulted in a softer material (low G' values). The amount of crystallized material was not affected by sonication, which indicates the softer network obtained is due to the increase of crystal size. Power ultrasound used in this research showed a considerable effect on the changing of microstructure of high saturated shortening, which might have a further application in food industry.

EAT 1.1/FS&FF 1: Confectionery Fats, Cocoa Butter, and Related Topics on Crystallization

Chair(s): N. Widlak, ADM Cocoa, USA; R. Campos, Mars Chocolate North America, USA; and D. Rousseau, Ryerson University, Canada

The Effect of Pressure and Volume on Fat Phase Behavior: Important But Often Overlooked System Variables. R.W. Lencki, R.J. Craven, University of Guelph, Guelph, ON, Canada

A large body of scientific knowledge currently exists on the crystallization behavior of triacylglycerols (TAGs). Systems range in composition from highly-purified synthetic compounds to complex multicomponent natural fats. A typical phase diagram displays melting behavior as a function of composition and temperature, and assumes minimal contributions from pressure and volume since neither variable is measured or controlled. While this approach may be appropriate for many TAG systems, there are situations where pressure and volume may play a significant role in fat crystallization (e.g. measuring the porosity of chocolate with pressurized mercury, compression and rarefaction in ultrasound). Pressure and volume can also be a factor at high solids concentrations once a fat crystal network has formed within the sample, a situation that is commonly found in many fat systems. Under these conditions, the solid matrix can constrain the volume of the occluded liquid phase, leading to internal pressures that can, at least transiently, be significantly different from the surrounding atmosphere. In this work, thermodynamic equations developed to characterize the effect of pressure and volume on TAG solid-liquid equilibrium will be used to explain a number of industrially important fat crystallization phenomena.

Early-stage Crystallization of Cocoa Butter Influenced by Different Emulsifiers. P Podchong¹, S Sonwai¹, D Rousseau², ¹Department of Food Technology, Faculty of Engineering and Industrial Technology, Silpakorn University, Thailand, ²Department of Chemistry and Biology, Ryerson University, Toronto, Canada

The purpose of this research was to investigate the early-stage crystallization kinetics, microstructure and polymorphism of cocoa butter (CB) in the presence of 5 wt% sorbitan esters (trioleate, monooleate, tristearate, monostearate or monopalmitate) or canola oil. Microstructure was investigated via polarized light microscopy, crystallization kinetics with pulsed NMR and DSC and polymorphism with simultaneous SWAXS/DSC (Hecus S3-

MicrocaliX). Sorbitan tristearate had the largest effect on CB early-stage crystallization, likely co-crystallizing with POS and SOS and accelerating its initial crystallization, but retarding its crystal growth and polymorphic transformations. This was presumably due to the molecular complementarity of the stearic acids present in the CB and surfactant. There was a lesser, though still notable, influence of both sorbitan monostearate and monopalmitate whereas sorbitan trioleate and monoleate as well as canola oil had little effect given their liquid state at all temperatures. The palmitic and stearic-based surfactants reduced CB crystal size with these same surfactants accelerating initial crystallization rate (or nucleation), but leading to lower equilibrium SFCs. DSC revealed that these surfactants primarily modified the crystallization of CB's high-melting fraction. Overall, it was shown that sorbitan esters can significantly impact cocoa butter crystallization, though this is highly-dependent on surfactant structure.

Surfactant Complementarity and Confined Gap Shear to Control Triglyceride Crystallization and

Microstructure in Oil-Continuous Systems. S. Ghosh^{1,2}, D. Rousseau², ¹University of Saskatchewan, Saskatoon, Saskatchewan, Canada, ²Ryerson University, Toronto, Ontario, Canada

Confined gap cooling was used to generate novel lipid microstructures and water droplet encapsulation matrices. Hydrogenated canola oil (HCO) in canola oil with or without the presence of surfactants [glycerol monooleate (GMO), polyglycerol polyricinoleate (PGPR)] was cooled from 70° to 25°C at a constant shear rate (400 s⁻¹) in the parallel plate geometry (500 µm gap) of a controlled-shear rheometer. Different-sized and shaped HCO crystal aggregates were observed depending on the distance from the parallel plate centreline. The lowest linear shear velocity (nearest the centerline) promoted spherulite-spherulite clustering into spheroidal aggregated masses with rough surfaces ~150 µm in length. Under mid and high-shear conditions, crystal-crystal clustering was observed around a central spherulite. The resulting spheroids had a smoothed surface and became smaller with gradually higher shear (down to ~40 µm in length at high shear). Freshly-prepared 20 wt% water-in-oil emulsions consisting of the same oil phases as above and cooled under the same shear/temperature conditions were tested for their capacity to encapsulate the dispersed phase. HCO crystal spheroids made with GMO-stabilized emulsions encapsulated nearly all dispersed water droplets whereas with PGPR-stabilized emulsions, no droplets were incorporated as all droplets remained in the continuous oil phase. Comparative bulk-cooling with an impeller-type mixer did not lead to the development of such microstructures nor any water droplet encapsulation. This demonstrated the vital requirement of a confined gap for the development of these shear-induced microstructures.

Influence of Cocoa Butter Diacylglycerols on the Isothermal Crystallization of Cocoa Butter. Nathalie De Clercq¹, Sabine Danthine², Koen Dewettinck¹, ¹Ghent University, Ghent, Belgium, ²Université Gembloux Liege, Gembloux, Belgium

In this study a multi-methodological approach was used to study the isothermal crystallization, of cocoa butter in the presence of maximum 10% cocoa butter diacylglycerols over a period of four hours. At an isothermal temperature of 20°C, CB crystallizes in a two-step process: the α crystals formed during the first step transform to β' in the second step. DSC, pNMR, oscillatory rheology, XRD and PLM were used for this purpose.

Influence of Monopalmitin on the Crystallization Behaviour of Palm Oil. Stefanie Verstringe¹, Sabine Dhantine², Frédéric Depypere¹, Veerle De Graef¹, Koen Dewettinck¹, ¹Ghent University, Ghent, Belgium, ²University of Liege, Gembloux, Belgium

Emulsifiers, present by nature or added on purpose, are known to affect the crystallization and thus also the macroscopic properties of fats. Effects on all crystallization levels (nucleation, crystal growth, polymorphic transitions, network formation, sintering) as well as on fat crystal size and morphology are reported. However, research on the influence of emulsifiers on the crystal size and crystal morphology, microstructural development and macroscopic properties of crystallized fat systems is still in its infancy. Therefore, a multi-methodological analytical approach was used in this research to gain more insight into the effect of monopalmitin on the palm oil crystallization behaviour. The blends were crystallized at different temperatures ranging from 15 to 28°C. pNMR and DSC were applied to characterize the primary crystallization behaviour. Next to primary crystallization, microstructural development and macroscopic properties were evaluated by oscillatory rheology. Polarized light microscopy was used to follow the

development of the fat crystal networks. XRD measurements were used to elucidate the polymorphic behaviour of the blends. From the results, it can be concluded that a monopalmitin concentration as low as 1% already has a clear effect on the palm oil crystallization behaviour.

Characterization by Rheo-NMR and Modeling of a Crystallizing Triglyceride Mixture. M. Li, G. Mazzanti, Dalhousie University, Halifax, NS, Canada

Shear flow affects the solid content (SC) and nanoparticle size of fats. Binary mixtures of pure Triolein and Trimyristin in a ratio of 7:3 were diluted to 60% in non-crystallizing Triolein. 40% 7L3M was cooled at 10°C/min from the melt at 60°C down to several temperatures between 12°C and 24°C. The samples were crystallized at each temperature either statically or under shear rates of 800, 80, and 8 s⁻¹. The sample cell combined a rheometer with a nuclear magnetic resonance (NMR) spectrometer to measure SC values. Viscosity and total mechanical energy delivered were precisely measured by the rheometer. The measurements were compared to common equations describe the dependency of viscosity on solid volume fraction, to understand the effect of orientation of the crystallites at higher shear rates. Most of the results were described accurately by the Arvami model whereas in some of them the presence of two regimes was observed, where diffusion controlled growth dominated the later times. The small values of the intrinsic viscosity were observed at high shear rate showing that the particles were small in size compare to low shear rate, which supports the hypothesis that shear reduces the particle size.

Rheo-NMR Study of the Structural Consequences of Shear Variation during the Crystallization of Milk Fat. G. Mazzanti^{1,2}, ¹Dalhousie University, Halifax, NS, Canada, ²Institute for Research in Materials, Halifax, NS, Canada

The effect of shear variations on the crystallization of milk fat was investigated using Rheo-NMR. Previous Rheo-XRD experiments had demonstrated that the variation in applied shear rate during crystallization had modified the size of the final nanoplatelets in different fats (G. Mazzanti et al., Cryst. Growth Des., 11 (10), 4544-4550). To further investigate the structural consequences of this size modification, milk fat samples were crystallized under two continuous and two discontinuous shear profiles, at a common temperature. The crystallizing colloidal suspensions displayed a shear thinning time-dependent rheological behavior, consistent with the expected. The final solid fraction was affected by the type of shear profile applied. It was correlated to the Rheo-XRD integrated intensity values, demonstrating the effect on the proportionality factors that nanoplatelet aggregation/segregation and orientation have under shear. At the end of the shear profile the structures were allowed to set and were monitored during a short period of time using oscillatory Rheo-NMR. The four profiles resulted in different visco-elastic time-profiles of the materials. These properties were consistent with the modification of solid content and the Rheo-XRD observations of nanoplatelets size change.

Use of Time-resolved X-ray Diffraction to Monitor the Difference in Phase Transformation Trajectories of Tags Containing Oleic and Stearic Acids, as a Function of Symmetry and Cooling Rate. Laziz Bouzidi, Suresh S. Narine, Trent Centre for Biomaterials Research, Departments of Physics & Astronomy and Chemistry, Trent University, Peterborough, Ontario K9J 7B8, Canada

The thermal and polymorphic evolutions associated with crystallization of pure triacylglycerols (TAGs) with Oleic and Stearic Fatty Acids were monitored using a laboratory X Ray Diffractometer, allowing time-resolved X-ray diffraction at both wide and relatively small angles as a function of temperature (XRDT). These measurements were performed in combination with high sensitivity differential scanning calorimetry (DSC) carried out at two widely different cooling rates in the -90 to +90°C range. It was found that the combination of these techniques allowed the thermal monitoring of TAG polymorphism even at relatively high cooling rates of 3°C/min. The formation of α , β' and β phases, and their transitions were followed simultaneously by DSC and XRDT, facilitating the identification of the thermal events recorded. The large influence of molecular symmetry on crystallization and evolution of polymorphism of TAGs with Oleic and Stearic Fatty Acids was demonstrated, and has significant implications for the crystallization of cocoa butters sourced from different geographies and altitudes with varying TAG symmetries involving oleic and stearic acids.

MORNING

EAT 2: Lipid Structures - Fundamentals

Chair(s): N. Garti, Hebrew University of Jerusalem, Israel; and B. Kickle, ADM Food Oils Research, USA

Triacylglycerol Polymorphism is a Stereochemical Phenomenon. R.J. Craven, R.W. Lencki, Department of Food Science, University of Guelph, Guelph, Ontario, Canada

The physical properties of foods containing fat are often dependent on the polymorphism of constituent triacylglycerols (TAG). For example, chocolate is more appealing when its fat component is in form V rather than form VI, likewise, margarines in the β' form are preferred over those in the β form. In the current literature, the role of stereochemistry in TAG polymorphism is seldom considered. Yet, the link between stereochemical arrangement of molecules in the unit cell and polymorphic form of solid TAG is unmistakable — in general, β -form unit cells contain both stereoisomers whereas β' -form unit cells contain only one stereoisomer (JAOCS, DOI:10.1007/s11746-011-1952-3). This observation is based on results from studies of crystalline tendency via the binary phase behavior of chiral TAG enantiomers and crystallographic space group determinations of β - and β' -tending TAG. Consequently, any plausible descriptive mechanism for TAG polymorphism must take unit cell stereochemistry into account. In fact, when the stereochemical orientation of constituent molecules is considered, the descriptive mechanism for TAG polymorphism is vastly improved. For instance, observed differences in polymorphic behavior for enantiopure and racemic TAG including the β' -stability of enantiopure systems are easily explained from this new perspective.

Emulsifier Effects on Fat Crystallization as Influenced by Hydrogen Bonding with Triglycerides. V. Kamara¹, S. Ghosh^{2,1}, D. Rousseau¹, ¹Ryerson University, Toronto, Ontario, Canada, ²University of Saskatchewan, Saskatoon, Saskatchewan, Canada

The possible role of hydrogen bonding on fat crystallization was investigated in model systems consisting of glycerol monooleate (GMO) and hydrogenated canola oil (HCO) mixed with either canola oil (CO) or mineral oil (MO). The former oil consists primarily of unsaturated triglycerides whereas the latter consists of straight and branched alkanes, with a key difference between these oils being the presence of carbonyl groups in CO that can potentially hydrogen bond with hydroxyl groups in GMO. Crystallization kinetics and equilibrium solid fat contents (SFCs) were determined via pulsed NMR, microstructure was examined using polarized light microscopy and combined SWAXS/DSC was used to establish HCO polymorphism and crystallization onset. Under the experimental conditions used, GMO had little influence on HCO crystallization kinetics when combined with CO. However, when mixed with MO, GMO significantly suppressed HCO's rate of crystallization and yielded a higher equilibrium SFC compared to the GMO-free HCO-MO mixture. Combined SWAXS/DSC experiments revealed that GMO delayed the early-stage appearance of HCO's wide-angle spacings in both CO and MO. Polarized light microscopy confirmed the impact of GMO on HCO crystallization, particularly when mixed with MO. IR spectral characterization revealed that GMO with its abundant hydroxyl groups formed hydrogen bonds with the ester carbonyl groups in CO, rendering it less available to alter HCO crystallization. However, in MO, there was no such hydrogen bonding between the emulsifier and the surfactant possible, given the lack of carbonyl groups in MO alkanes. Hence, GMO greatly influenced HCO crystallization. Overall, this study demonstrated that a contributing factor to understanding the crystallization kinetics of triglycerides lies in their possible hydrogen bonding with emulsifiers.

Models for Tailoring Fat Products under the Nanocrystalline Paradigm. G. Mazzanti^{1,2}, ¹Dalhousie University,

Nanocrystalline platelets, hypothesized from shear crystallization experiments, have been proven to be the basic building blocks of fat networks. Some general trends of the effects of supersaturation and shear rate on their characteristics are now known, and some new questions have arisen. What models can we use to combine the main variables that we need for structuring our materials? How do we develop new products and processes from this knowledge? Recent experiments and theoretical developments show new possibilities to tailor the thermal, rheological and oil binding characteristics of the fat. For any given formulation we need to account for: * Nucleation and growth rate (as usual), but also agglomeration/segregation and limiting nanocrystalline platelet size * Modification of polymorphism and phase composition (nanostructure) by applied shear * Heat generated when using very high shear rates for novel products * Formation of concentration gradients and thermal gradients as a function of applied shear. * Superficial forces, modifiable by small amounts of specialty lipids * Creation of structures through different agglomeration nanoscale pathways in both the liquid continuum and the solid network

Polymorphic Behavior of Sunflower Oil Stearins. J.A. Rincon Cardona¹, Y. Ye², S. Martini², R.J. Candal^{1,3}, M.L. Herrera^{3,4}, ¹University of San Martín, School of Science and Technology, San Martín, Buenos Aires, Argentina, ²Utah State University, Logan, Utah, ³National Research Council of Argentina (CONICET), Buenos Aires, CABA, Argentina, ⁴University of Buenos Aires, Faculty of Exact and Natural Sciences, Buenos Aires, CABA, Argentina

The actual legislation about *trans* fats encouraged manufacturers to find *trans* fats alternatives. Very recently, a new variety of sunflower oil has been cultivated in Argentina. This mutant line has a high stearic content (17 to 22%) on a high oleic background. Its stearins have appropriate physical properties to use in chocolate. However, the polymorphism of this new material which is closely related to chocolate shelf life and consumer acceptability was not described yet. Two sunflower stearins obtained by dry or solvent fractionation, were melted and then crystallized at 10°C/min to different crystallization temperatures. Isothermal crystallization was followed using synchrotron radiation X-ray. In both cases, the α -form is obtained after a few minutes for all crystallization temperatures selected (5, 16, 18.5 and 19°C for soft stearin and 10, 23, 24, and 25°C for hard stearin). When samples were in the α -form solid fat content was lower than 3% but when polymorphic transition to more stable forms occurred they started to crystallize very rapidly. Hard stearin showed two different β ' forms while soft stearin presented only one β ' form. β -form did not crystallize under the experimental conditions used in this study. To obtain it samples were stored at -20°C for a month.

Surface Structure Observation on Growing Fat Crystals Examined with Optical Microscope. Hironori Hondoh¹, Gen Sazaki², Kiyotaka Sato¹, Yoshinori Furukawa², Satoru Ueno¹, ¹Hiroshima University, Higashi-Hiroshima, Hiroshima, Japan, ²The Institute of Low Temperature Science, Hokkaido University, Sapporo, Hokkaido, Japan

Understanding of fats crystallization is a key to control physical functionality of fats in many technological applications. The fat crystallization has been studied with DSC, X-ray diffraction, SFC, etc., however, the fat crystallization process in molecular level is still unclear. In this study, we have performed molecular-level in situ observation of growing fat crystals in dodecane solution, using laser confocal microscopy combined with differential interference contrast microscopy (LCM-DIM). This novel technique has already been applied to ice and protein crystals (1, 2), and we aimed at applying it to fat crystals. We observed the surface of a tripalmitin beta form crystal having thin needle shape in supersaturated solution with LCM-DIM. We found the following results; 1) The surface of the crystal was not smooth at the molecular level, showing grooves along the direction parallel to the long edge of needle-shaped crystals. 2) The step movement on the crystal surface was anisotropic. The growth rates of the steps moving along the long edge of the crystal were higher than those along the short edge. The present study has shown that the LCM-DIM is a new tool to monitor the elementary processes the fat crystallization in diluted solution. 1. G. Sazaki, et al., PNAS. (2010). 2. G. Sazaki. et al., J. Cryst. Growth, (2004).

Effects of Matrix Nanostructure on Oil Migration using Magnetic Resonance Imaging Technique. Farnaz Maleky¹, Alejandro Marangoni¹, Kathryn McCarthy², Michael McCarthy², ¹University of Guelph, Guelph, Ontario, ²

Canada, University of California, Davis, Davis, California, USA

The effects of processing conditions and the nano- and meso-scale structure of crystalline materials on oil migration was quantified using Magnetic resonance imaging (MRI). Three methods were used to prepare the crystallized cocoa butter: static, seeded and sheared and spatial and temporal changes of the liquid lipid content was monitored in a 2-layer model system of cocoa butter and a model cream filling. The rate of oil migration was quantified by a kinetic expression based on the linear dependence of oil uptake by cocoa butter and the square root of the time. Samples showed distinctly different rates of oil migration. The relationships between the structural factors (nanoparticle size, domain size, tortuosity and particle distribution) and the permeability coefficients suggest that shear crystallization can significantly reduce oil migration.

Effect of High Intensity Ultrasound on Crystal Morphology, Melting Profile, and Viscoelastic Properties of a Low-saturated Shortening. Yubin Ye, Suyapa Padilla, Silvana Martini, Utah State University, Logan, UT, USA

Previous research in our laboratory has shown that high intensity ultrasound (HIU) can change the functional properties of lipids. The objective of this research was to evaluate the effect of HIU on the microstructure, melting profile and viscoelastic properties of a low-saturated shortening. Results from this research show that HIU can be used to induce the crystallization at low supercoolings and generate small crystals as evidenced by polarized light microscopy and scanning electron microscopy. The crystal network obtained using these crystallization conditions are characterized by a higher elasticity (higher G') and a sharper melting profile. The amount of crystalline material was not affected by sonication, suggesting that the harder network obtained is due to the presence of smaller crystals. HIU did not generate oxidation products in the lipid and did not change the chemical composition in terms of triacylglycerol and fatty acid methyl ester composition. Moreover, no changes in the polymorphic form of the crystal network were observed as a consequence of sonication. The effect of ultrasound on the crystallization behavior of lipids might be due to cavitation events and/or localized high shear forces created during the crystallization process.

The Determination of the Free Energy of Mixing During Crystallization of Triacylglycerol Binary Mixtures. O. Al-Qatami, G. Mazzanti, Dalhousie University

Upon crystallization, TAGs self-assemble in many nano and micro crystalline structures (phases) characterized by different melting points, enthalpies and heat capacities as well as molecular packing arrangements. These arrangements are different polymorphs and solid-solution phases that cannot be physically separated due to their nanocrystalline nature. However, determination of the proportions between those phases and their phase compositions is necessary to model their behavior. This determination remains a big challenge for food engineers and researchers because the phases cannot be separated, and since they form solid solutions, we have an infinite number of possible compositions. In fact, it is enough to change the cooling rate of a particular mixture to obtain a different combination of phases. To tackle the challenge, the energies that determine how TAG molecules interact with each other to form a crystalline phase must be determined. The main objective of our study is therefore to estimate the excess energy of mixing of TAGs. The enthalpy of crystallization and heat capacity of the crystalline phases must be determined very accurately to be able to measure the deviations that account for the excess energies.

Oils in Nanospace Confinement. D.A. Pink^{1,3}, E. Papp-Szabo², M. S. Razul¹, C. J. MacDougall¹, F. Peyronel³, A. G. Marangoni³, C. B. Hanna⁴, ¹Physics Department, St. Francis Xavier University, Antigonish, NS, Canada, ²Physics Department, University of Guelph, Guelph, ON, Canada, ³Guelph-Waterloo Center for Graduate Work in Physics, Department of Food Science, University of Guelph, Guelph, ON, Canada, ⁴Department of Physics, Boise State University, Boise, ID 83725-1570, USA

Crystalline nanoparticles (CNPs) constitute the fundamental supramolecular structural units of many polycrystalline lipid networks and their aggregation is a key step in the process of network formation [Acevedo & Marangoni, *Cryst. Growth Des.*, 2010, 10, 3327. Acevedo et al. *Curr. Opin. Coll. Interface Sci.*, 2011, 16, 374. Pink & Quinn, *J. Roy. Soc. Chem. Food & Function* 2011 (in press)]. Understanding the physical states of oils in nanospaces between CNPs is likely essential to understanding the rheological properties and oil binding capacity of such materials, and enables rational searches for substitutes for trans-fats. We have used atomic scale MD to model triolein between

tristearin CNPs and showed that, as the CNP separation decreased, triolein exhibited stable density oscillations and was expelled from between the CNPs [Pink et al. Submitted Oct. 2011]. This might have consequences for industries seeking to replace trans-fats. We have extended our modeling to oil mixtures comprising triolein and oils derived from replacing cis chains by trans chains to study whether (a) phase separation arises in oils between CNPs, (b) oil is expelled selectively from between CNPs, (c) oil density oscillations arise. Various cis-trans ratios will be modelled. The results will provide a basis for designing reduced-trans-fats components in foods.

AFTERNOON

EAT 3: Lipid Structures - Applications

Chair(s): D. Kim, Kraft Foods Inc., USA; and P. Rousset, Nestle Research Center, Switzerland

Crystallization Behavior of Structured Lipids by Chemical Interesterification of Palm Stearin, Coconut Oil and Canola Oil. Fabiana Andreia Schafer De Martini Soares, Roberta Claro da Silva, Jessica Mayummi, Jivaldo do Rosario Matos, Luiz Antonio Gioielli, University of São Paulo, São Paulo, São Paulo, Brazil

A lot of food products contain a substantial amount of fat, of which a significant part is present in the crystallized form. One of the main functions of fat in food products is its contribution to the structure of the product. Many of the sensory attributes such as spreadability, mouth feel, snap of chocolate, texture are dependent on the mechanical strength of the underlying fat crystal network. The palm stearin and coconut oil, are often being used in foods such as margarines, shortenings and confectionery products, due to the number of desirable properties that they impart to the finished products, including chemical composition, high oxidative stability and plasticity at room temperature. The main goal of present research effort was evaluate the behavior of crystallization of blends of palm stearin coconut oil and canola oil in different proportions. Structured lipids were synthesized with individual fats (palm stearin, coconut oil and canola oil) and their blends by chemical interesterification. The crystal structure was analyzed by DSC and polarized light microscopy at temperatures of 25°C.

Effect of Ripening Time on Partial Coalescence and Butter Grain Aggregation in Cream. P. Buldo, L. Wiking, Aarhus University, Tjele, Denmark

The temperature treatment of cream is the time-consuming steps in butter production. A better understanding of the mechanisms leading to partial coalescence, such as fat crystallisation during butter manufacturing, will contribute to optimization of the production process. In this study, the mechanisms of cream crystallisation during churning of the cream, including the effect of ripening time were investigated in order to understand how churning time and partial coalescence are affected. Crystallisation mechanisms were studied as function of time by oscillation rheology, by differential scanning calorimetry and by nuclear magnetic resonance. Microstructure formation was investigated by oscillation rheology and particle size distributions. The obtained results showed that viscosity measurements can be used to monitor partial coalescence, thus formation of butter grains during churning of the cream in a rheometer cell. Ripening time influenced both churning time and final viscosity of the cream; longer ripening time resulted in larger butter grains. Furthermore, it was shown that the mechanisms leading to partial coalescence are based on the crystallisation of the high melting faction in the continuous phase rather than the amount of solid fat content.

Effect of Storage Temperature and –period on Crystal Inversion Mechanisms and Water Droplet Size Distribution in Table Spreads. Stine Rønholt¹, Jacob Judas Kain Kirkensgaard², Kell Mortensen², Jes Christian Knudsen¹, ¹Department of Food Science, Faculty of LIFE Sciences, University of Copenhagen, Copenhagen, Denmark, ²Department of Basic Sciences and Environment, Faculty of LIFE Sciences, University of Copenhagen, Copenhagen, Denmark

Crystalline fat phases exist in numerous food and pharmaceutical products. The nano- and microstructural properties of fat crystals, for example chain packing, polymorphism, crystal size and aggregation behavior determines the quality of these products, especially texture and rheological properties. We studied table spreads consisting of anhydrous milk fat, rapeseed oil (RO) and water, and followed crystal growth and transitions during storage at technologically relevant temperatures. Using x-ray and DSC we investigate crystallization mechanisms and thermodynamic behaviour of fat the crystals. Crystal interactions in spreads are quantified by rheology. The solid fat content is linked to the rheological profile. Confocal Laser Scanning Microscopy (CLSM) visualized microstructural features of the samples. Water droplets sizes are measured during storage and their changes related to stability and properties of the crystalline fat phase. Our data shows, that storage between 5°C and 20°C decreases the hardness (measured at 5°C) of the spreads about 2–fold and increases water droplet sizes compared to samples stored continuously at 5°C. Addition of RO to the system made this effect more pronounced. Furthermore, CLSM images reveal that addition of RO changes the crystal size and shape.

Partial Coalescence and its Importance in Ice Cream. R.W. Hartel¹, M.M. Warren², P. Spicer², ¹Department of Food Science, University of Wisconsin, Madison, WI, USA, ²Procter&Gamble, West Chester, OH, USA

Partial coalescence, or the clustering of fat globules, provides ice cream with its rigidity, creaminess, and stability and is considered to be a primary factor affecting melt-down rate. Emulsifier level and type, total percent fat, type of fat, and the whipping of mix into ice cream govern partial coalescence and the degree of fat globule aggregation. However, the exact mechanism(s) of partial coalescence remains elusive, in part, due to the inability to observe two globules as they interact. Recent studies using a micro-manipulator technique have shown that fat crystals extending through the fat globule interface into the aqueous phase are not needed for partial coalescence of fat globules. In model systems, particles at the interface (Pickering emulsions) or within the interior of the droplet exhibited a range of behavior from either no coalescence to complete coalescence. Between these two extremes were conditions where coalescence was partially arrested by the solid phase. These new findings will be discussed in the context of partial coalescence in ice cream.

Waxes as Organogelator for Soybean Oil. H.S. Hwang, S. Kim, M. Singh, J.K. Winkler-Moser, S.X. Liu, NCAUR, ARS, USDA, Peoria, IL, USA

This research reveals that a small amount of a food grade plant wax may replace a large amount of the hardstock containing trans-fat or saturated fat. Natural waxes including plant waxes and animal waxes were evaluated for the gelation ability toward soybean oil (SBO) and compared with hydrogenated vegetable oils, petroleum waxes and commercial non-edible gelling agents. Sunflower wax (SW) and rice bran wax could make a gel with concentrations as low as 0.5 wt%. Gelation ability of a wax is significantly dependant on its purity and detailed composition. A wax ester with longer alkyl chains has significantly better gelation ability toward SBO than that with shorter alkyl chains indicating that the chain length of a component in a wax such as wax ester is an important factor for gelation ability. The SW-SBO organogel showed increased melting point with increased SW content. The effects of cooling rate on crystal size and firmness of a gel were investigated. The dependence of firmness on cooling rate was so significant that the desired texture of an organogel could be achieved by controlling the cooling rate in addition to controlling the amount of gelling agent.

Thixotropic Ethylcellulose Oleogels. T. Stortz, A.G. Marangoni, University of Guelph, Guelph, ON, Canada

Ethylcellulose (EC) is able to gel oils; however these gels may break and lose functionality when shear is applied. Therefore, this research focussed on developing a strategy for imparting EC oleogels with thixotropic properties. Gels were prepared with EC, various oils, and various surfactants by heating all ingredients in a beaker with mixing until the EC dissolved (between 110-150°C). The viscosity of the set gel was determined using a rheometer with cone and plate configuration. It was found that gels made with approximately 1:1 (w/w) oil:surfactant ratios were thixotropic. Similar results were observed with different oils however, changing the surfactant led to great changes in the viscosity and proportion of viscosity recovery of the gels. It was also found that the viscosity of the gel could be modified by changing the concentration or molecular weight of the EC. Furthermore, the viscosity of the gel was found to increase

with decreasing density of the oil phase. The combination of oil and surfactant in a specific ratio has been used successfully to produce an EC thixotropic oleogel. This development will prove beneficial when utilizing oleogels in food, particularly, cosmetic systems.

Stability of Wax/oil Self-assembled Materials as Affected by Oil and Wax Composition. Nicholas Chiew, Chin Yiap Tan, Suyapa Padilla, Silvana Martini, Utah State University, Logan, UT, USA

The objective of our research was to evaluate the effect of wax and oil type on the formation of oleogels. Sunflower, bees and paraffin waxes were used to form gels in corn, sunflower, soybean, safflower, canola, and olive oils. When wax concentrations below 1% were used, a liquid-like soft material was obtained. Interestingly, depending on the oil and wax type some of the materials showed phase separation. The phase separation was quantified using a light scattering equipment. In addition, the morphology of the crystals formed was studied using polarized light microscopy. Results show that phase separation was a function of type of wax and concentration. When sunflower oil waxes were used at concentrations of 0.25%, phase separation was observed in sunflower, canola, and corn oil, but not in olive, soybean, and safflower oil. Similarly, when sunflower, bees and paraffin waxes were crystallized in soybean oil, sunflower wax did not show phase separation at 0.25% while beeswax showed phase separation, and paraffin wax was completely soluble. Results obtained in the polarized light microscope suggest that a network of needle-like wax crystals needs to be formed to obtain a liquid-like material that is resistant to phase separation.

Development of a Response Surface to Tailor the Mechanical Properties of Edible Oil Oleogels for a Diverse Range of Applications in Food Systems. A.J. Gravelle, S. Barbut, A.G. Marangoni, University of Guelph, Guelph, Ontario, Canada

In recent years, the structuring of edible oils using the polymer ethyl cellulose (EC) has become an active area of research. These so-called "oleogels" have been shown to have serious potential for applications in food systems as a substitute for fats which are rich in trans- and saturated fatty acids. Applications for EC-based oleogels which are currently being investigated include chocolate, cream filling, and frankfurter-type products, among others. EC-based edible oil oleogels can be made to have vastly different mechanical properties depending on the formulation used, but their employment in new food systems will require a much broader knowledge of the physical properties of these oleogels. To this end, we have explored how the mechanical and textural properties of these gels are affected by a variety of factors; oil type, concentration of EC, viscosity of EC (related to molecular weight of the polymer chains), and addition of a surfactant at several EC-to-surfactant ratios. Response surfaces are being used to characterize these properties to aid in the selection of appropriate gel formulations for a wide range of food applications in which structured edible oil may be used as a replacement for saturated and trans-fat rich ingredients.

Formulation of *trans*-free Special Shortening and Semi-solid Fat for Production of Chocolate-filled Cookies. F. Madadnoee^{1,2}, M.R. Modalal^{1,2}, F. Karami¹, H. Pour Rahman³, M. Rashidian⁴, ¹Agri-Industry & Veg. Oil of Mahidasht,(A.I.V.M.Co.), Kermanshah, Iran, ²Kesht Va Sanat Shomal(KVSS), Mazandaran, Iran, ³Shirin Vatan Cookies company, E. Azarbaijan, Iran, ⁴Agriculture and food industry faculty of research and science of Azad univercity, Tehran, Iran

There was a need for two different types of fats and oil products for manufacturing chocolate-filled cookies. First the shortening with high plasticity which could be passed through 12-16 nozzles in two different colors and they would join together after passing through the nozzles. Second the creamy filling which was made by semi-solid fat. We formulated *trans*-free shortening for coating of cookies. Shortening was made with different bases of palm fractions, hydrogenated palm oil, liquid oil and monoglyceride. Semi-solid fat was formulated by liquid oil and hydrogenated palm oil, monoglyceride and sorbitan tristearate (STS). Shortening and semi-solid fat were used in two plants. Consumer companies approved the replacement of their traditional high trans product with the new formulation. Taste and texture were evaluated by sensory analysis and proved to be superior to the traditional product. Fatty acid profile of shortening: SFA 49.3%, MUFA 35.6%, PUFA 13.9% and trans 0.5% and for semi solid fat: SFA 30.5 MUFA 33.8, PUFA 34.4 and trans 0.5%

New Family of 75% Reduced-fat Olestra Shortenings for Bakery Applications - Elimination of Post-hardening.

P. Lin, D. Back, D. Applyby, R. Berger, L. Wen, Procter and Gamble Company, Cincinnati, Ohio, USA

Heart disease and diabetes remain key medical issues. A family of 75-100% reduced-fat olestra shortenings can part of a set of useful tools to combat these issues with recent GRAS approval of olestra for baked goods. P&G Foods Ingredients developed five new olestra shortenings with these benefits: low sat fat (8-12% versus ~50% in zero-trans shortenings), zero trans fat, and significant caloric reduction (75-100%). These shortenings used a new patent-pending intermediate-melting-fraction (IMF) olefin component with a steep SFC curve and minimal solids at body temperature. These shortenings contained palm oil that caused post-hardening resulting in rheological firmness of the shortenings to increase 3-5 times over six months (commercially undesirable). This paper reports on the reformulation effort to eliminate the post-hardening effect. The new olestra IMF components and a saturated diglyceride (structuring agent) are key components of these shortenings that simultaneously deliver excellent baking and taste performances with significantly improved nutritional values. The melting profiles and plasticities of these new shortenings are compared to their zero-trans counterparts using SFC and rheometry. These new shortenings have been utilized in a variety of baked performance tests with excellent results and a selected few examples will be presented.

WEDNESDAY

MORNING

EAT 4/S&D 4.1: Dispersions, Emulsions, and Foams

Chair(s): A. Wright, University of Guelph, Canada; and C. Rojas, AMCOL, USA

Role of Conformation and Interactions of Hybrid Silicones at Various Interfaces. Ponisseril Somasundaran¹, Parag Purohit¹, Somil Mehta², ¹Columbia University, New York, NY, USA, ²Dow Chemicals, Mumbai, Maharashtra, India

Hybrid silicones are unique due to their distinct simultaneous hydrophobic and hydrophilic properties. Behavior of non-ionic and ionic silicone polymers at various interfaces suggested conformational transition of silicone chains from a linear to a coiled form, that are controlled by interfacial concentrations and interactions with bulk phases. At the oil-water interface, functional groups of silicone polymers interact with water phase whereas siloxane backbone interacts with the oil to form O/W emulsion, with the size distribution and charge of it attributed to play an important role in modifying properties of substrates such as fabrics. With a bimodal droplet distribution of silicone emulsions, the nano-sized droplets can penetrate deeper into the substrate to provide bounciness, while macro-sized droplets can coat the top layer leading to friction reduction. Using Atomic Force Microscopy, we observed the treated cellulose fibers are uniform, well stacked and smoother than the untreated fibers. Spectroscopic analysis of treated fibers using Raman spectroscopy indicates a decrease in fiber stress as a function of modification of silicone polymer and the interaction pH. Our study demonstrates that behavior of hybrid silicones at various interfaces can be tailored by selecting appropriate functional modifications.

Effects of Phase Behavior on Spontaneous Formation of Emulsions/Nanoemulsions and on Emulsion Destabilization. C.A. Miller, Rice University, Houston, Texas USA

Knowledge of equilibrium phase behavior is important for understanding various aspects of emulsion behavior. Recent results using dynamic light scattering are presented showing how both initial morphology and drop size of emulsions/nanoemulsions formed on diluting a w/o microemulsion made with an anionic surfactant differ greatly depending on salinity of the brine used for dilution. The differences are directly related to the effect of salinity on oil-

brine-surfactant phase behavior. Possible applications in forming aqueous dispersions of nanoparticles and in detergency are discussed. The effect of phase behavior in breaking of emulsions is reviewed for emulsions stabilized by surfactants and by compounds such as asphaltenes in crude oil. When solid particles contribute to emulsion stability, addition of suitable inorganic salts or surfactants can often alter the particles' wettability, causing them to leave the interface, which can destabilize the emulsion. Recent examples of this mechanism are shown.

Enzyme-Triggered Aroma Release from Emulsions. B.C. Wong, R.J. Elias, J.D. Lambert, J.N. Coupland, The Pennsylvania State University, University Park, PA, USA

Fine ($d \sim 200$ nm) sodium caseinate-stabilized eicosane-in-water emulsions were equilibrated with ethyl octanoate (EO) at 28°C as either supercooled liquid droplet emulsions or crystalline solid lipid nanoparticles. Porcine trypsin (0.25%) was added to digest the protein and the destabilization of the dispersions and headspace concentration of EO were measured over time. In the absence of enzyme, liquid droplet emulsions had a lower headspace concentration of EO than solid droplet emulsions (0.5 $\mu\text{L}/\text{mL}$ vs. 3.5 $\mu\text{L}/\text{mL}$). When the liquid droplets were treated with protease there was a steady increase in both droplet size and solid fat content over time as the caseinate was digested and the supercooled droplets began to coalesce and crystallize. After a delay there was a sudden increase in headspace EO associated with the complete crystallization of the eicosane. Solid droplet emulsions were destabilized by protease but there was no corresponding change in solid fat constant or headspace EO. This model system study demonstrates the use of supercooled liquid droplet emulsions as delivery vehicles for hydrophobic solutes with release triggered by the action of digestive enzymes. While the present work is focused on flavor release there are potential applications for nutrient as well as pharmaceutical compound delivery.

Salt Release from Fat Crystal-Stabilized Water-in-Oil Emulsions. S. Ghosh¹, M. Nadine², D. Rousseau³,
¹University of Saskatchewan, Saskatoon, Saskatchewan, Canada, ²AgroSup, Dijon, France, ³Ryerson University, Toronto, Canada

Fat crystal-stabilized water-in-oil (W/O) emulsions were developed as a controlled release matrix for the delivery of salt (NaCl). Emulsions were prepared at 70°C by homogenizing 20% (w/w) water, canola oil, emulsifiers and stabilizing fat, which were then cooled with stirring and stored at room temperature. Glycerol monostearate (GMS), glycerol monooleate (GMO) or polyglycerol polyricinoleate (PGPR) were used as emulsifiers and hydrogenated canola oil (HCO) was added as a continuous phase stabilizer. The release of salt from the water droplets towards the external aqueous phase was measured at room temperature and under heating using a conductivity meter dipped into a glass beaker containing DI water and emulsion stirred at 300 rpm for 2 hr. Pickering-stabilized emulsions (GMS-CO) had the highest encapsulation efficiency (only 2.7% of the total salt released) while GMO-HCO-CO emulsion (partial Pickering and network stabilization) showed highest salt release (24%). Interfacial GMS crystals formed solid shells around water droplets preventing diffusion of salt molecules. In the GMO-HCO-CO emulsion, the presence of water droplets with partial or no interfacial fat crystal coverage led to higher salt release compared to GMS-stabilized emulsions. Both GMS and GMO emulsions showed rapid release of their salt load upon melting of surrounding fat crystals. The PGPR-HCO-CO emulsion, with its smaller droplet size distribution compared to the GMO-HCO-CO emulsion, showed much less salt release (3.6%) confirming the significant influence of emulsion stability and droplet size in controlling encapsulation efficiency of salt in W/O emulsions.

The Influence of Alcohol on Foam Behavior. S.T. Adamy¹, C.F. Neller², ¹Church & Dwight Co., Inc., Princeton, NJ, USA, ²Rutgers University, Piscataway, NJ, USA

Control of foam is typically managed by the addition of materials which are either meant to destabilize the foam lamellae by migrating to the film surface and disrupting the film, or by interfering with molecular coherence at the air-water interface. Low molecular weight materials like octanol have been reported to stabilize or destabilize such coherence, depending on the system, resulting in enhanced or reduced foam stabilization. This study examines the effect of various isomers of octanol on the foaming properties of detergent systems containing an anionic and nonionic surfactant. Studies were performed by use of a SITA R-2000 foam tester, which employed an agitator to produce foam. Studies were performed in both a dynamic way, where the volume of foam was monitored during generation, and in a static way, where the collapse of the foam over time was observed. It was found that foam behavior was

dependent on a number of factors, including the concentration of the octanol isomer, as well as the presence of other materials, like salts, in the system. Differences were seen between systems where the octanol was pre-solubilized in the system and when the octanol was added during foam generation. In the case of pre-solubilization, no foam impairment and even slight stabilization was seen, while injecting the octanol during generation resulted in immediate foam collapse.

Bio-compatible Low Salinity Triglyceride Microemulsions and Detergency. L.D. Do, D.A. Sabatini, The University of Oklahoma, Norman, OK 73019, USA

Vegetable oil (VO)-based microemulsions (MEs) have wide applications in pharmaceuticals, foods, consumer and personal care products. Due to the hydrophobicity and bulky structure of VO, formulating bio-compatible, alcohol free and low salinity VO-based MEs is challenging at best. Pioneering study in our group was able to form alcohol free VO-based MEs using extended-surfactants (surfactants with internal polypropoxylate and/or ethoxylate groups) and achieved high canola oil detergency. However, the required salinity concentrations ranged from 8-14 wt% eliminates the practical use of these formulations. In this work, we will present our development on bio-compatible VO-based MEs with mixed surfactant/linker systems at low salinity concentration (<0.9 wt%) with algae and canola as model oils. Effect of biorenewable surfactants (i.e. sophorolipids, chitosan) on VO-based MEs will be discussed. All ME types were achieved using bio-compatible mixed surfactant/linker systems at less than 0.9 wt% salinity and 0 to 0.5 wt% extended-surfactant at ambient temperature; to our knowledge, reported here for the first time. Solubilization enhancement of some hydrophobic drugs using these MEs will be presented. More than 90% canola oil detergency was achieved within 10 minute at low surfactant concentration (150 ppm), demonstrating the effectiveness and robustness of our formulations.

Effect of Emulsifiers on Micro-and Nano-structural Changes of Shear Sensitive Emulsions. M.B. Munk^{1,2}, M.L. Andersen², A.G. Marangoni³, ¹Palsgaard A/S, Juelsminde, Denmark, ²University of Copenhagen, Department of Food Science, Frederiksberg C, Denmark, ³University of Guelph, Department of Food Science, Guelph, Ontario, Canada

Rheological properties of o/w-emulsions made from palm kernel oil were strongly influenced by low-molecular-weight emulsifiers. Addition of lactic acid ester of monoglyceride (LACTEM) yielded highly viscous emulsions. However, viscosity was reduced drastically by stirring at 5 °C, whereas stirring at room temperature caused a large increase in viscosity. The process was reversible since viscosity could be decreased again by stirring at cold temperatures. Mixtures of LACTEM and saturated monoglyceride yielded low-viscosity emulsions which also exhibited a sudden shear-thickening behaviour at room temperature. Addition of unsaturated monoglyceride to LACTEM generated a very firm emulsion that was not sensitive to shear or temperature. Confocal microscopy suggested that increased viscosity was due to fat aggregation. Despite shear-induced structural changes, fat polymorphism in the emulsions did not change, but remained in β form. On the other hand SAXS spectra showed a distinct change as emulsions went from liquids to thick pastes: The intensity of the 001 peak increased dramatically. Transmission electron microscopy suggested that fat did not maintain a globule structure; instead it was converted into large plates. Moreover proteins, which initially were located at the interface of fat globules, seemed to create a thin network in the water phase when emulsions thickened.

Physical Control of Fat Crystallization in O/W Emulsion-type Chocolate under Shear. Kiyotaka Sato, Masashi Ochi, Hironori Hondoh, Satoru Ueno, Hiroshima University, Higashi-Hiroshima, Japan

In general, fat crystallization in oil-in-water (O/W) emulsion occurs under quite complicated conditions, and various external factors are affecting the fat crystallization in oil droplet and at the water-oil interfaces. In this study, we observed the effects of shear on the polymorphic crystallization of cocoa butter in O/W emulsion, which is mimic to ganache-type chocolate. Such type of chocolate is produced without tempering process after formation of O/W emulsion at elevated temperature under high shear. We observed that, without the shear, cocoa butter crystallizes in a metastable form IV. However, the application of shear during the controlling process caused direct crystallization into form V, whose melting point is higher than that of form IV and thereby favored for chocolate. We will present the fat crystallization without and with shear under different crystallization conditions.

AFTERNOON

EAT 5: General Edible Applications Technology

Chair(s): G.R. List, USDA Consultant (Retired), USA; and B. Farhang, University of Guelph, Canada

Challenging Endogenous Oil Components. Roman Przybylski, University of Lethbridge, Department of Chemistry and Biochemistry, Lethbridge, Alberta, Canada

Edible oils are utilized in a variety of foods as ingredient and as medium for food preparation including cooking and frying. The main components forming oil are triacylglycerols however a variety of endogenous minor components are also present and affect its performance and stability. During processing, preparation and storage oil components are affected mainly by oxidative degradation the main source of off-flavor and detrimental compounds. Besides oxidation, the variety of other processes is involved in degradation of oil and food components. This talk provides a brief overview on oil endogenous components and formation during processing and food preparation of compounds negatively impacting quality of food products and its nutritional value. Each of degradative processes will be related to the oil composition, stability and performance at standard processing conditions including possible approaches to prevent unwanted components formation.

Phytosterol Solubility in Lipid Vesicles of Phosphatidylcholine and its Relationship to Stability. Nuria C. Acevedo, Alejandro G. Marangoni, University of Guelph, Canada

The physical properties of bio-membranes have intrigued researchers for many years. In this report, we focus on phytosterol esters solubility within unilamellar membranes of phosphatidylcholine (PC) and the characterization of the mixed membranes. Vesicles containing lipids in ratios of 1:X phosphatidylcholine (PC):phytosterol esters were generated by microfluidization. Size and morphology of the vesicle membranes were determined by light scattering and Cryo-TEM respectively. X-ray scattering was used to determine vesicle structural parameters as well as the presence of phytosterol crystals. Furthermore, Polarized Light Microscopy (PLM) was carried out to image the phytosterol crystals in vesicle samples at different storage times. Characterization of the vesicle size distribution and Cryo-TEM, demonstrated that the vesicles are homogeneous in size (~150nm) and are primarily unilamellar. Additionally, the presence of phytosterol esters led to an increase in the bilayer thickness, relative to pure PC due to its incorporation within the bilayer. PLM micrographs revealed the presence of crystals of vesicles directly after microfluidization confirming a solubility limit of 40-50 mol% phytosterol in PC membranes.

Stability Evaluation of the Sucrose Laureate-stabilized Phytosterol Nanodispersion-containing Soy Milk. Wai Fun Leong¹, Chin Ping Tan², Yaakob Che Man², Oi Ming Lai³, Kamariah Long⁴, Mitsutoshi Nakajima⁵, ¹School of Science, Monash University, Sunway Campus, 2-5-23, Jalan Lagoon Selatan, 46150, Bandar Sunway, Selangor, Malaysia., ²Department of Food Technology, Faculty of Food Science and Technology, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia., ³Department of Bioprocess Technology, Faculty of Biotechnology and Biomolecular Sciences, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia., ⁴Malaysian Agricultural Research & Development Institute (MARDI), P.O. BOX 12301, 50774 Kuala Lumpur, Malaysia, ⁵Graduate School of Life and Environmental Sciences, University of Tsukuba, Tennoudai 1-1-1, Tsukuba, 305-8572, Japan

This work was initiated to investigate the stability of phytosterol nanodispersion-fortified soy milk over a period of 12 weeks in terms of mean particle size (PS) and distribution, viscosity and appearance. The soy milk was used as a model for delivery of phytosterol nanodispersion, while autoclave was conducted as a measure of preservation of the phytosterol nanodispersion-soy milk mixed. The phytosterol nanodispersions showed a stable PS and distribution and

appearance over a 12-week storage period. The autoclave treated nanodispersions experienced an increase in PS, changes in distribution profiles and a decrease in the total phytosterol concentration during storage. Soy milk fortified with phytosterol nanodispersions exhibited a higher mean particle size than its non-fortified counterpart, but there were no significant differences ($p > 0.05$) in appearance between soy milk and nanodispersions-fortified soy milk, at least for the first 8 weeks of storage. The fortified phytosterol nanoparticles were observed to become entrapped into the fat droplets of the soy milk. The apparent viscosity of all experiment samples decreased during storage.

Factors Affecting the Oxidative Stability of Omega-3 Emulsions Prepared with Milk Proteins. A.F. Horn, N.S. Nielsen, C. Jacobsen, Division of Industrial Food Research, National Food Institute, Technical University of Denmark, Denmark, Kgs Lyngby, Denmark

Omega-3 fatty acids are prone to lipid oxidation due to their unsaturated nature. In oil-in-water emulsions, lipid oxidation is expected to be initiated at the oil-water interface. The properties of the emulsifier used and the structure at the interface are therefore expected to be of great importance for the resulting oxidation. This presentation will give an overview of parameters that are expected to change the properties and structure of milk protein components at the interface of 10% fish oil-in-water emulsions. Results from three different studies will be included. The first study compared the effect of two different high pressure homogenizers on oxidation in caseinate and whey protein isolate emulsions. The second study evaluated the effect of homogenization pressure and temperature on emulsions prepared either with whey proteins or a combination of caseinate and β -lactoglobulin. Finally, the third study investigated the influence of pH on emulsions prepared with α -lactalbumin, β -lactoglobulin or a combination of the two. In all three studies the adsorption of individual protein components were shown to be of great importance to lipid oxidation. Thus, the effect of various conditions for emulsion production will be discussed in relation to protein adsorption and the structure at the interface.

A Chemometric Approach for Finding the Relevant Fatty Acids Contributing to the Melting Fractions of Milk Fat. P. Buldo, M. Krogh Larsen, L. Wiking, Aarhus University, Tjele, Denmark

Melting behavior and fatty acid (FA) composition of cream from four farms for a total of 33 cows were analyzed. Multivariate data analysis was used to identify the FAs which contribute the most to the melting fractions, and to differentiate between creams from practical feeding regimes. Feeding influences the fatty acid composition of milk which influences the melting behavior of milk fat. We demonstrated that the melting point of the medium melting fraction was positively correlated to palmitic acid (C16:0), while it was negatively correlated to oleic acid (C18:1cis9), conjugated linoleic acid (CLA cis9 trans11 or rumenic acid), vaccenic acid (C18:1 trans11), elaic acid (C18:1trans9) and myristoleic acid (C14:1). The melting behavior was related to specific FA present in minor amounts as well as the two major fatty acids present in milk. Thus, the position of the FA in the glycerol molecules plays an important role. The melting point of the high melting fraction could not be related to FA composition. The FA composition of cream proved to be a good parameter to differentiate milk from different feeding strategies, moreover the individual cow variation was observed in the score plot. This study introduced a fast, indirect and successful chemometric method to investigate the relationship between FA and melting point.

Synthesis and Characterization of *trans*-free Margarine Fat Analogs by Enzymatic Interesterification of Cottonseed Oil and Palm Stearin. G. Pande, Casimir C. Akoh, University of Georgia, Athens, GA, USA

trans-Free interesterified fat was enzymatically synthesized from palm stearin and regular cottonseed oil for possible use in margarine formulation. Response surface methodology (RSM) was used for optimization. The independent variables were substrate molar ratio (2-5), temperature (50-65 °C), time (6-22 h), and lipases (Lipozyme® TLIM and Novozym® 435). Incorporation of stearic acid (mol %) was the dependent variable. A good-fit model was constructed using regression analysis with backward elimination. Desirable products composition were achieved at 57 °C, 14 h, 1:4, using Lipozyme TLIM, with 5.66 mol% stearic acid and at 56 °C, 6 h, 1:4.75, using Novozym 435, with 5.89 mol% stearic acid. Using optimal conditions, structured lipids (SLs) were synthesized in a 1 L stir-batch reactor and characterized for fatty acid profile, positional analysis, TAG species, polymorphism, solid fat content, and melting/crystallization profiles. Solid fat contents at 25 °C were lower for SLs (29.8 ? 33.2%) than the corresponding physical blends (38.7 ? 40.2%). Novozym 435 catalyzed SL had desirable fatty acid profile, physical properties, and suitable β' polymorph. This SL could be used as margarine fat analog and an alternative to partially hydrogenated fat.

Reduced Saturated Fatty Acids Solutions for Confectionery Fats without Compromises to Process and Product Functionalities. Morten Daugaard Andersen, Bjarne Juul, AAK, Aarhus, Denmark

For decades the aim of reducing or eliminating trans fatty acids in confectionery products has been a major theme in lipid research. More recently a demand for non-hydrogenated products for cleaner labelling were added to the agenda in many confectionery markets. At present, the growing nutritional focus on confectionery fats with reduced content of saturated fatty acids (SAFA) presents a significant technological challenge for the confectionery fats producers. The manufacturers wish to reduce the SAFA content without any sacrifice to process and product functionalities for the finished confectionery product. Novel breakthroughs in lipid technologies and understanding of how lipids function in confectionery applications have resulted in a series of confectionery products with reduced SAFA content ranging from spread fats, filling fats and coating fats. Special focus on the challenges to develop a non-hydrogenated CBS with reduced SAFA content will be discussed.

Microalgae as an Alternative Source of Omega 3 Fatty Acids? E. Ryckebosch, K. Muylaert, I. Foubert, Katholieke Universiteit Leuven KULAK, Kortrijk, Belgium

Numerous epidemiological, animal and clinical studies have shown that the long chain omega 3 polyunsaturated fatty acids (LC-PUFA) EPA and DHA are effective in preventing or treating several diseases, such as cardiovascular disorders and cancers, and that they play a role in brain and nerve development of growing fetuses and infants. However, in many Western countries, the current average intake of these LC-PUFA is below the recommended level. This raises interest in food supplements containing LC-PUFA on the one hand and food stuffs enriched with LC-PUFA on the other hand. Currently, the main commercial source of LC-PUFA is fish oil. However, several problems are associated with these oils: unpleasant odor, contamination with heavy metals, presence of cholesterol, geographical and seasonal variation in quality, as well as increasingly stringent regulation of fisheries. The aim of this research is to investigate the possibilities of microalgae as an alternative source of these LC-PUFA. The composition of the algal oil (from different species) in comparison with already commercially available sources will be discussed. Attention will be paid to the form in which the LC-PUFA are present, the presence of other nutritionally interesting compounds such as phytosterols and the oxidative and hydrolytic stability of the oil.

Edible Applications Technology Posters

Chair(s): G.R. List, USDA (Retired), USA; and G. Cherian, Kelloggs North America, USA

Study on the Oil Absorption of Fried Instant Noodle in Several Vegetable Oils.

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Frying instant noodle is very popular because its special flavor, taste, feasibility to store and so on. However, its high oil content increases both food cost and the risk of the obesity and coronary heart diseases. Thus, it is highly desired to reduce oil in fried instant noodle. This work studied the total oil absorption, surface oil absorption and moisture content of instant noodle frying in several vegetable oils, included soybean oil, rapeseed oil, cottonseed oil, high oleic sunflower oil, palm oil (33°C), palm olein (24°C), palm stearin (52°C). The result showed the total oil content in the fried instant noodle in rapeseed oil was lowest, followed with cottonseed oil. And the surface oil uptake of the instant noodle fried in rapeseed oil was also lowest. The moisture content and the total oil uptake of fried instant noodle were inverse correlation. According to the condensation mechanism, removing of water could create pores which absorb oil in cooling process. It was also found that there was no obvious linear correlation between total oil uptake and some index property of these vegetable oils, such as FAC, viscosity and saponification value.

Microencapsulation of an ω -3 oil in a Trehalose Matrix.

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It is well known that stability of lipids is improved by encapsulation since it is a physical means offering protection against oxidation without the need of antioxidants. A concentrated from fish oil, mainly from salmon, rich in DHA (C22:6), EPA (C20:5), and DPA (C22:5) was encapsulated by freeze-drying emulsions. The selected emulsifier was sodium caseinate at 0.5, 2, and 5 wt% levels. The matrix was trehalose, a known cryoprotectant, which was used at 20 or 30 wt% level. The ability to retain the core material with time was studied by measuring the extractable and non extractable fat of the different formulations. Efficiency of encapsulation was strongly dependent on formulation. The 20 wt% trehalose, 5 wt% sodium caseinate powder had a retention efficiency of 80%. This powder has a water content of 5%. Its matrix was in the amorphous state. The mean volume diameter of particles ($D_{4,3}$) was smaller than those of the other formulations. Besides, $D_{4,3}$ of the reconstituted emulsion showed no significant differences compared to the original emulsion $D_{4,3}$, showing that freeze-thaw did not affect initial droplet size distribution. This emulsion was stable at least for 1 week and its structure showed individual droplets evenly distributed.

Effects of Oxidation on the Mechanical Properties of Canola Oil-based Ethyl Cellulose Oleogels.

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The structuring of edible oils using polymers or via the self-assembly of small molecules has great potential for applications in food systems. Of particular interest in our laboratory is the gelator molecule ethyl-cellulose (EC) which, upon heating above its glass transition temperature ($\sim 140^{\circ}\text{C}$) and subsequent cooling, forms a polymer network capable of entrapping liquid oil. These oleogels have potential applications as a fat mimetic, however the high temperatures required to achieve gelation can have a negative effect on the oil-phase as a result of heat-induced auto oxidation. The mechanical properties of canola oil-based EC oleogels both with and without the surfactant sorbitan monostearate (SMS) were evaluated using back extrusion. It was discovered that in the presence of SMS, the formation of primary oxidation products during gel preparation can result in a significant increase in the mechanical strength of the resulting oleogels. This work may provide insight into the molecular interactions at play within EC oleogels and also help improve the quality of vegetable oil-based EC oleogels for applications in food systems.

Crystallization Behavior of Blends Formulated by Neural Networks with Interesterified Fats from the Melt Point and SFC of Commercial Fats for Use in Hard Margarines.

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The formulation of fats by neural networks has been an alternative for industries, specially in the manufacture of the low trans products, with the use of interesterified fats. However, in the process of blending is necessary the evaluation of the crystallization behavior of blends due to the influence on technological characteristics and stability. This study had as objective to evaluate blends formulated by neural networks with interesterified fats and soybean oil, using as standard commercial fats indicated for hard margarines. The blends were formulated by a neural network, trained with SFC and MP data of raw materials, through the solicitation of responses based on MP and SFC of the commercial fats. The products were evaluated for fatty acid composition and triacylglycerol, SFC and MP, isothermal crystallization by NMR and crystallization behavior by DSC. Experimental SFC and MP were very similar to these predicted by neural network. Differences were found between SFC of neural network and commercial blends, mainly at 10, 20 and 45°C and MP. The crystallization isothermal showed that the blends formulated, in general, had more fast crystallization than the commercial fats, while the crystallization curves obtained by DSC were very similar.

Composition-Structural-Textural Relationships in *n*-Alkane Mixtures used by the Food and Pharmaceutical Industry.

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The aim of the present investigation is to establish simple relationships among structural properties of pure *n*-alkanes

(C24 to C32) with the thermo-mechanical properties of complex commercial *n*-alkane mixtures (CM) used by the food and pharmaceutical industry. Based on SAX and WAX measurements obtained in pure *n*-alkanes, binary and ternary mixtures, and in the CM we established that, at room temperature (25°C) a single orthorhombic crystal organization was developed in the CM. In agreement with reports in the literature, this multi-*n*-alkane crystal organization has a lamellar structure with a molecular stacking identity (i.e., long *c* parameter) corresponding to a chain length of a hypothetical orthorhombic organization with a carbon atom number approximately equal to the average carbon atom number (\bar{n}) of the multi-*n*-alkane commercial mixtures. Both, the chain length and the \bar{n} of this hypothetical orthorhombic organization showed simple relationships with the melting temperature, hardness, and stickiness of the CM crystallized at 25°C. Our results showed that simple structural parameters associated with the crystal structure of *n*-alkanes may be used to predict the physical properties of complex mixtures of *n*-alkanes that finally determine their functionality in food and pharmaceutical products.

Phenols, Melanoidins, and Antioxidant Activity in Green and Processed Coffee Beans from *Coffea arabica* and *Coffea canephora*.

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Coffee beans represent a natural source of phenols, which may decrease during roasting; however other compounds, such as melanoidins, are formed. Four Arabica coffees (green, torrefacto, italian, and french roast), and two Robusta coffees (green and instant) were evaluated. Phenols were identified and quantified. The antioxidant activity was evaluated (ABTS•+ and DPPH•). Melanoidins were determined spectrophotometrically. The phenols identified were rutin, chlorogenic, caffeic and ferulic acids. For coffees from Arabica no significant differences ($p > 0.05$) were observed on the antioxidant activity of green beans and processed coffees. However, torrefacto coffee presented a significantly greater ($p < 0.05$) antioxidant activity (238.71 $\mu\text{mol trolox/mg}$) than french and italian roast coffee (198.07 and 202.68 $\mu\text{mol trolox/mg}$, respectively). The improvement of the antioxidant activity in torrefacto coffee could be due to formation of melanoidins. Melanoidin content was significantly higher in roasted coffee beans than in green Arabica beans. In the case of instant coffee from Robusta coffee, phenolic content and antioxidant activity increased threefold. It can be concluded that coffee is a good source of antioxidants, which can be found naturally in coffee beans and are formed during roasting.

W/O Organogelled Emulsions Stabilized with Candelilla Wax.

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Organogelled W/O emulsions were stabilized with candelilla wax (CW). Emulsions were prepared with 20% of distilled water and 80% of lipid phase containing high oleic safflower oil with 2 or 3% of CW, and 0.25 or 0.5% of monoglycerides (MG). Both phases were mixed and homogenized (200 bar) at 70°C, and quickly cooled up to 47°C to develop the wax organogel in the continuous phase. Emulsions were analyzed after storage (24 h) at refrigeration temperature (5°C). Stability of the emulsions was analyzed by visual inspection, texture analysis, polarized light micrographs and sedimentation test. Emulsions presented a white-yellowish color, no apparent phase separation was observed in the samples. All the systems presented a solid like behavior. Emulsion's texture increase with the CW content, but it was independent on the concentration of MG. On the other hand, texture of emulsions was contrasted against the texture of organogels with the lipid phase composition used in emulsions. Systems with 2% of CW presented similar texture in the emulsion and organogel. But, systems with 3% of CW emulsions were twice hard than the organogels. To our best knowledge, this is the first report on the stabilization of spreadable W/O emulsions stabilized with wax organogels.

Rheological Properties of Fats Formulated with Soybean Oil and Interesterified Soybean Fats.

J.M. Block¹, B. Mattioni¹, K. Gandra², D. Barrera-Arellano², A. Marangoni³, ¹Santa Catarina Federal University, Florianopolis, Santa Catarina, Brazil, ²Campinas State University, Campinas, Sao Paulo, Brazil, ³University of Guelph, Guelph, Ontario, Canada

The macroscopic rheological properties of the fat crystal networks are of extreme importance for different applications. Fats for puff pastry margarines and biscuit fillings are formulated to a high solids' content in order to ensure a good performance in the finished product. In this work, the rheological properties and melting profile of zero-trans fats for biscuit fillings and puff pastry formulated with blends of soybean oil and interesterified soybean fats were investigated and compared to commercially available fats. Samples with soybean oil/fat blends were formulated using an artificial neural network and prepared in a Gerstenberg and Agger crystallizer. The rheological properties (the storage modulus - G' ; and loss modulus - G'') were determined using small deformation dynamic rheology and the melting profile was determined using Differential Scanning Calorimetry. Our results suggest that samples formulated with blends of soybean oil and interesterified soybean fats showed lower storage and loss modulus and melting temperatures compared to standard fats. Although fats formulated with blends of soybean oil and interesterified soybean were softer than commercial roll-in shortenings, they had physical properties such that lamination could still be successfully carried out.

The Impact of Lemon Oil Composition on Formation and Functional Properties of Nanoemulsions.

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Lemon oil is a complex organic compound isolated from citrus peel, which is commonly used as a flavoring agent in beverages, foods, cosmetics and household products. In this study, the functionality of lemon oil-in-water nanoemulsions formed by four different types of lemon oils was studied. The composition and physicochemical properties (density, interfacial tension, viscosity) of the lemon oils were characterized. Single-fold (1x) lemon oil contained > 90% monoterpene hydrocarbons, whereas 10-fold (10x) lemon oil contained three main classes: 35% monoterpenes; 14% sesquiterpenes; and, 33% oxygenates. Oil composition affected the solubilization and stability of lemon oil nanoemulsions in the presence of non-ionic surfactant micelles. The movement of oil molecules from oil droplets to surfactant micelles increased with increasing lemon oil fold. Droplet growth occurred in nanoemulsions formed by 1, 3, or 5x lemon oil due to Oswald ripening and coalescence. This study provides important information about the relationship between lemon oil composition and its performance in nanoemulsions suitable for use in the food and beverage industries.

Nutraceutical Lipid Substances in Various Korean Rice Cultivars.

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The levels of nutraceutical lipid substance in the 23 cultivars of Korean rice were investigated. The nutraceutical lipid substances tested were tocopherols (tocopherols and tocotrienols), phytosterols, policosanols, and γ -oryzanol. A wide range of tocopherol level was detected in the 23 cultivars (range 14.9~38.2 mg/kg rice). Four tocopherol isomers, *i.e.*, α -, β -, γ -, and δ - tocopherol and three tocotrienol isomers, *i.e.*, α -, γ -, and δ -tocotrienol were identified, whereas no β -tocotrienol was detectable. The major tocopherols in the 20 cultivars were α -tocopherol and α -tocotrienol, while that in the 4 cultivars namely *Segyuejinmi*, *Hanareum*, *Dasan No.1*, and *Chunseok* was γ -tocotrienol. The phytosterol levels of 23 cultivars varied from 295.0 mg/kg rice in *Dearip* to 492.0 mg/kg rice in *Kuennun* and the major phytosterol was β -sitosterol in all cultivars. The policosanol level in *Boramchan* cultivar was highest as 51.5 mg/kg rice, while that in *Dearip* cultivar was lowest as to 18.0 mg/kg rice. There were no significant difference in γ -oryzanol levels of all cultivars.

Control of Crystallization of Diacylglycerols.

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Diacylglycerol (DAG) has beneficial effects on obesity and obesity-related diseases, therefore widespread application of DAG to food products has been expected. In general, for use of fatty materials in food products, it is important to know and control the crystallization behavior of them, because it greatly affects the physical properties of the final product. In the previous study, we investigated crystallizing process of DAG made from vegetable oil (DAG-rich oil), in which 1,3-disaturated DAG (1,3-SS), 1,3-saturated-unsaturated DAG (1,3-SU), and 1,3-diunsaturated DAG (1,3-UU) separately crystallized in a sequential manner. In this study, we examined the way to regulate the crystallization of DAG-rich oil. We found that polyglycerol fatty acid esters (PGFEs), which are well-known as edible crystal

modifiers, could inhibit the early stage crystallization of DAG. Predominant crystallizing components in this stage were 1,3-SS and 1,3-SU. And as a consequence of it, the overall crystallization of DAG-rich oil, including crystallization of 1,3-UU, was retarded very effectively. These results indicated that controlling the crystallization of 1,3-PP and 1,3-PO would be very important for various application of DAG., and that adding of PGFE might be one of the ways.

Crystalline Phase Compositions from a Triacylglycerol Blend: Data and Model.

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The description and modeling of the complex phase behavior in fats begins with understanding of pure triglycerides that compose them coupled with knowledge of kinetics of nucleation, growth and equilibrium phase composition. We compared the theoretical and experimental phase composition during non-isothermal crystallization of trilaurin and trimyristin mixtures. Small and wide angle time resolved synchrotron X-ray diffraction were used to investigate polymorphism and composition under static conditions. Theoretical compositions were estimated using the Linear Kinetic Segregation model (LKS) (Los and Flöter, 1999) while varying the kinetic constants ratio and excess free energy parameters. To compute the experimental compositions, an empirical correlation was determined that estimates solid phase composition as a function of d-spacing for single and mixed phases at the end of cooling. Statistical tools employed in modeling process of d-spacing and intensities included iterative optimization procedures. A first approximation for the experimental solid phase composition was estimated as a product of the linear proportion of molecular length by an anchored function of tilt angle. Parameters of the LKS model were optimized to enable a comparison between the theoretical prediction and the experimental estimation of solid phase composition.

Polymorphism and Microstructure of Fats Formulated with Soybean Oil and Interesterified Soybean Fats.

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Currently, formulation of cost-competitive trans-free fats with similar functionality to their trans-containing counterparts is a major challenge facing the food industry. In this work, the polymorphism and microstructure of zero-trans fats for biscuit fillings and margarines for puff-pastries formulated with blends of soybean oil and interesterified soybean fats were investigated and compared to commercially available fats. Samples with soybean oil/fat blends were formulated using an artificial neural network and prepared in a Gerstenberg and Agger crystallizer. The polymorphism and microstructure of the fats were determined using X-Ray Diffraction and Polarized Light Microscopy. Oil-binding capacity was also evaluated. Results showed the molecular packing of triacylglycerols in the fat crystals was different among the samples. Fats for biscuit fillings were in β form, while puff-pastry margarines were in β' and β forms and commercial samples were in β' form. In all samples, small crystals were observed ($< 2.0 \mu\text{m}$ for biscuit fillings and $< 3.0 \mu\text{m}$ for puff-pastry margarines) with thin, needle-shaped morphology. Samples with larger crystals displayed greater oil losses than samples with smaller crystals. Microstructural features (shape and size of crystals) of fats formulated with soybean were found to be similar to commercial fats.

A Comparative Study of Waxes as Oil-Binding Materials.

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The oil-binding and network structuring capabilities of organogels makes them not only suitable as trans and saturated fat alternatives for many food products, but also as stabilizing agents in cosmetic and pharmaceutical applications. Oleogels are defined as organic liquids encapsulated by a three-dimensional gel network formed through the self-assembly of organogelator molecules present at low concentrations. One of most promising systems to date is that of vegetable waxes dispersed in oils at concentrations ranging from 1-4% (w/w). Several wax sources are available commercially, however, a systematic comparative study of their physical properties is lacking. Rice bran (RBX), sunflower (SFX), candelilla (CLX) and carnauba (CRX) wax were molten into canola oil at 0.5-90% concentrations and allowed to crystallize at room temperature for 24 hours under static conditions. The critical concentration for the different waxes were 0.5% for both SFX and RBX, 2% for CLX and 4% for CRX, suggesting a greater structuring

power for SFX and RBX. Bright field light microscopy revealed ~40-65 and 50-90 μm needle-like structures in RBX and SFX, respectively, ~20 μm needle aggregates in CLX, and ~50 μm spherulites for CRX. Differential scanning calorimetry on 10% wax in oil showed single sharp melting peaks for SFX ($T_p = 64^\circ\text{C}$) and RBX ($T_p = 72^\circ\text{C}$), while CLX and CRX displayed very broad peaks at 47 and 76°C , respectively. Wider melting peaks are indicative of a greater molecular heterogeneity in CRX and CLX. Small (SAXS) and wide angle (WAXS) powder X-ray diffraction studies demonstrated that chain packing conformation in all waxes was the same, with a characteristic β' configuration. SAXS studies showed, however, that only SFX and RBX exhibited ordered lamellar arrangement of wax molecules in the crystal, for both neat and diluted systems. Small deformation mechanical tests on the 10% wax in oil systems confirmed that the G' of the waxes followed the trend $\text{SFX} > \text{RBX} > \text{CRX} > \text{CLX}$ at room temperature. This study demonstrated that a greater molecular homogeneity leads to more efficient packing in the solid state and a greater crystalline order, which in turn creates a stronger network with greater structuring power. This increased structuring power and network strength results in greater oil binding capacity.

Crystallization and Polymorphism Behavior of Lipid Systems Containing Triacylglycerols Added Monoglycerides and Diglycerides.

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The study of crystallization and polymorphism behavior of a lipid system pure is of great scientific importance as a means of achieving understanding of the possible phenomena involved, which will provide basic knowledge to direct the addition or removal of these compounds in different raw materials. Thus, this project aims to study the effects of incorporation of LMs (MAGs and DAGs) to different TAGs also in pure crystallization and polymorphism of the same. For this purpose they are prepared mixed pure TAGs (tripalmitin, tristearin and triolein) with pure MAGs (monolaurin and monoolein monopalmitin) or with pure DAGs (diolein, and dipalmitin diestearin) in different proportions (1, 3 and 5%). The effects of addition of LMs will be observed by melting point, content solid fat, triacylglycerol composition, iodine and saponification index, regioespecific distribution, fatty acids, crystallization kinetics, thermal behavior, microstructure and polymorphism. Then the experiment will be conducted with purified palm oil added pure MAGs and DAGs and commercial (emulsifiers) in different proportions (1, 3 and 5%). At this stage of the project we studied the crystallization and melting behavior of commercial emulsifiers by differential scanning calorimetry (DSC) and polarized light microscopy (PLM).

Melting and Rheological Properties of Conjugated Linoleic Acid Rich Soy Oil.

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A conjugated linoleic acid (CLA) rich soy oil (CLARSO) has been produced by photo-isomerization of soy oil linoleic acid. The objective of this study was to compare melting and rheological properties of CLARSO relative to conventional soy oil. Soy oil containing 9.5%, 16.5% and 24% CLA was produced by soy oil linoleic acid photoisomerization. Changes in melting points and enthalpy were measured using differential scanning calorimeter and viscosity was measured using an AR 2000 Rheometer, in triplicate. Melting points of -40.2°C to -23.0°C for soy oil, -38.1°C to -10.5°C for 9.5% CLARSO, -36.8°C to -2.5°C for 16.5% CLARSO and -18.2°C to 2.4°C for 24% CLARSO were observed. Enthalpy (J/g) was 20.2 for soy oil, 19.8 for 9.5% CLARSO, 31.2 for 16.5% CLARSO and 34.4 for 24% CLARSO. The viscosity of CLARSO was higher than conventional soy oil and the viscosity increased as the CLA levels in the oil increased. 24.0% CLARSO had the highest and the conventional soy oil had the lowest viscosity. This study shows that CLARSO had higher melting temperature, enthalpy and viscosity relative to soy oil. The melting temperature, enthalpy and viscosity increased with increasing CLA levels.

Chemical Characteristics and Emulsion Properties of Cold-pressed Rice Bran Oil.

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Cold-pressed rice bran oil (CPRBO) is used in foods, cosmetics, and pharmaceuticals due to its desirable health and

functional attributes. The aim of this work was to study the nutritional benefits and emulsion properties of cold-pressed rice bran oil. The data showed that CPRBO contained a high content of vitamin E (0.93 mg/g oil), oryzanol (19 mg/g oil), phenolic content (14.70 mg FAE/g oil) and flavonoid content (7.54 mg CE/g oil). The major fatty acids in CPRBO are palmitic acid (20.1%), oleic acid (44.2%) and linoleic acid (30%). The influence of CPRBO (10-40%) and emulsifier (GMS) (1-5%) concentration on the properties of CPRBO were studied. We found that the mean droplet diameter, lightness (L^*) and yellowness (b^*) of CPRBO emulsion tended to decrease as GMS concentration was increased. However, the increasing of the GMS concentration had no impact on antioxidant activity, gamma oryzanol and total phenolic compound content of CPRBO emulsion. The storage of CPRBO emulsion at room temperature for 90 days showed that lipid oxidation was gradually increased after 30 days of storage as gamma oryzanol and antioxidant activity was decreased.

Functionality of Fats in the Formulation of Peanut Butter.

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Peanut butter is a popular product in Brazil for its excellent flavor and nutritional characteristics. However, despite their consumption patterns to follow established and rigidly set processes and quality, there may be changes in the consistency and reduced scattering characteristics, reducing the nutritional value and sensory quality. As a way to try to control these problems, fatty ingredients are used as promoters to improve stability and consistency, such as palm oil, palm stearin, palm olein, hydrogenated oils, mono and diglycerides. The aims to formulate peanut creams with peanut oil, palm fat and palm stearin in various proportions in order to obtain products more stable and consistent.

Shearing Does Determine Crystal size, Crystal Network Organization, and Rheology of Candelilla Wax Organogels.

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Most research involving organogelation has been obtained under static conditions. Preliminary experiments suggest that the application of shear to candelilla wax-safflower oil (CWSF) solutions under metastable conditions (52°C), enhance nucleation and crystal growth providing organogels with improved elasticity. The effect of shearing on the micro-structural and rheological properties of 3% CWSF organogels was investigated using: (1) static conditions during cooling (6°C/min) the CWSF solution from 90°C to 5°C, (2) constant shearing during cooling of the CWSF solution, and (3) shearing of the CWSF solution until achieving 52°C and then continuing cooling up to 5°C under static conditions. Shearing (10 to 100 rpm) was applied using a mechanical spectrometer. The application of constant shearing provided weaker gels ($G'' > G'$) as shearing rate increased. Using processing conditions as in (3) resulted in organogels with higher G' than the organogels developed statically, particularly using 50 rpm that also developed the larger crystals. Nevertheless, yield stress was higher in the organogels developed at 30 rpm. Shearing and the extent of its application as a function of supercooling determines crystal size and the proportion of transient to junction zones throughout the three-dimensional crystal network of the organogels.

Effect of Sun-drying and Pickling Process on Carotenoids and Tocopherols of Chilli Pepper (*Capsicum annuum* L. var. *glabriusculum*).

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Recent studies show evidence that peppers (*Capsicum sp.*) may be an important source of phytochemicals. However, it is known that preserving process may cause a marked loss. For this reason, the aim of this study was to compare in wild chilli pepper (*C. annuum* L. var. *glabriusculum*) the effect of two preserving methods: sun-drying (32 h at direct sunlight, 34-40°C) for red chilli pepper and pickling (5 min 100°C and pH 3.5) for green chilli pepper, on composition and antioxidant activity (ABTS•+ and DPPH•) of carotenoids and tocopherols. The results showed similar loss of total carotenoides for both process (28 and 32% respectively). In fresh red chilli pepper zeaxanthin and β -carotene were found; after sun-drying they decreased 62.2 and 39.4%, respectively. Respect fresh green chilli pepper, lutein, chlorophyll-a, chlorophyll-b and β -carotene were found. However, after pickling process only 86.4% of lutein and 81.2% of β -carotene were found. Among tocopherols α and γ were found. Both compounds in the sun-drying process

were increased. However, only 80% of α -tocopherol in pickling chilli was found. The antioxidant activity was lower when pickling was used than sun-drying process. These results show that temperature and pH had greater impact than drying time and sun light exposure.

Physicochemical Properties and Compatibility of Cocoa Butter-hardfats Blends.

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Hardfats, or fully hydrogenated oils, consist of materials with homogeneous composition, characterized by high melting point triacylglycerols. Although they are low-cost industrial products, the hardfats are considered relatively new materials, as they are unexplored in lipid technology. Some studies indicate that hardfats could behave as modulators of the crystallization process, acting as preferential nuclei for ordering the crystal lattice and inducing specific polymorphic habits, with great potential in seeding processes, mainly with a focus on the production of chocolates. This work evaluated the addition of different hardfats on the physicochemical properties of cocoa butter. Fully hydrogenated oils with significantly different chemical composition, obtained from palm kernel oil (FHPKO), palm oil (FHPO), cottonseed oil (FHCO), soybean oil (FHSO) and crambe oil (FHCrO), were evaluated. Blends of cocoa butter/hardfats, at concentrations of 1, 3 and 5% (w/w) were studied by determining the fatty acid and triacylglycerol compositions, melting point, solid fat profiles and iso-solid diagrams. Major changes on the melting point and solid profile were observed for blends containing FHSO. Except for the blends with FHPKO, there was no incompatibility between cocoa butter and the other hardfats. Blends with 1% of FHPO, FHCO and FHCrO proved to be suitable for use in chocolates.

In-situ Observation Crystallization Process of Cocoa Butter under Shear and Tempering.

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Crystallization process of cocoa butter (CB) is significant for chocolate processing. In chocolate producing, tempering process under shear is actually applied in passing CB in the tempering machine. However, no CB crystallization process has been studied under shear condition on tempering process. The purpose of this study is measuring the in-situ crystallization process under shear and tempering condition using by time-resolved synchrotron radiation X-ray diffraction. Additive effects of sugar and cacao mass in CB have also been studied on crystallization under shear and tempering. The shear speed was applied 400 revolution per second (400 revolution / sec) in all measurements. The major results are as follows; (i) shear stress accelerates the CB crystallization of form V, (ii) additives also promote the CB crystallization of form V, (iii) form V is appeared before tempering process of CB with sugar under shear. Ordering effect for rod-like shaped molecules under shear and heterogeneous nucleation with additives will be caused for the crystallization behavior described above.

Phase Behavior and Consistency of Soybean Oil Organogels Structured with Waxes and Vegetable Fat.

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Organogels prepared with vegetable fat (VF) based palm, sugarcane (SCW) and candelilla (CLW) waxes as structuring agents, and refined soybean oil as the immobilized phase were evaluated about the phase behavior and consistency (yield value) in samples crystallized statically at 5 and 25°C. Phase diagrams were constructed at different temperatures (5 to 35°C) and concentrations of structuring agent (waxes: 1 - 4%; VF: 5 - 25%, both w/w). On 5 and 10°C, was observed gels gelatinization with wax concentration from 1% (CLW) and 2% (SCW). The gels containing CLW presented gel structure up to 35°C only in formulations containing over 3% of wax, while the gels SCW presented gel structure up to 25°C in formulations containing over 3% of wax and over 20% of VF. Organogels containing CLW showed greater consistency in all formulations compared to gels containing SCW. The crystallization temperature of 5°C increased the gels consistency, except in the CLW organogel at concentrations above 3%. The results showed that VF contributed significantly to increasing the gels consistency only when they were crystallized rapidly (5°C). CLW gel showed higher gelatinization range in the concentrations and temperatures tested, when compared to SCW gel.

Edible Oils and their Relative Static Dielectric Values: What is There to Learn?

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Frequency dependent measurements of relative dielectric constants have been used by many authors as a way of evaluating frying oil qualities, as well as to detect adulterated vegetable oils. Measurements of dielectric values as a function of temperature and water content are generally performed in the frequency range of 100Hz to 500kHz. The capacitance of some edible oils was measured as the frequency's limit goes to zero using OSCAR, an instrument designed and built in our laboratories. The relative dielectric value ϵ_r can then be computed using this capacitance value. The relative permittivity is a complex quantity, $\epsilon_r(\omega) = \epsilon'_r(\omega) + i \epsilon''_r(\omega)$, that depends upon the frequency (ω) of the applied electric field. Observations indicate that in the DC limit ($\omega \rightarrow 0$) oils behave in ways not yet reported in the literature. We will discuss our observations and give an explanation as to how this can be of used in the quality control of commercial oils.

β -carotene Stabilization and Bioaccessibility from Non-surfactant Stabilized Lipid Particles.

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There is intense interest in the utility of lipid particles to stabilize and enhance the bioavailability of physiologically active molecules. β -carotene (BC, 0.1 wt%) was encapsulated within emulsion droplets (COE) and solid lipid nanoparticles (SLN) with Tween 20 (T20) or Poloxamer 188 (P188). BC had no impact on size (~ 130 nm), polymorphism, or melting behaviour. According to Cryo-TEM, the COE and SLN were spherically and platelet-shaped, respectively. Also, the P188 SLN were more angular and anisometric than the T20 SLN. The P188 SLN were exclusively in the β polymorph, while the T20 SLN contained β' and β . While the T20 COE and SLN were stable, flocculation occurred for the P188 systems after 90 days. BC stability was highest for the SLN and during dark storage at 4 (versus 20) °C ($p < 0.05$). Using an in vitro digestion model, all samples were stable during the gastric phase, but destabilized under fed state duodenal conditions. According to ζ -potential measurements, bile salts and phospholipids adsorbed rapidly to both solid and liquid interfaces, displacing the surfactant to a greater extent in the COE. Lipid digestion and BC bioaccessibility were much higher for the COE, with the SLN showing resistance to lipolysis.

Applications of Whey Powder in Sunflower Oil-emulsions Stability.

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Milk whey is a by-product from the cheese industry, generated in great amounts. During cheese manufacturing soluble whey proteins (primarily lactalbumins and lactoglobulins), lactose and minerals are drawn off in the whey. This by-product is generally processed by ultrafiltration and spray drying giving an interesting ingredient for the food industry. Dry whey has good functional properties such as emulsifying, water/fat holding, foaming, thickening or gelling capacity. The aim of this work was to study the stability of emulsions formulated with sunflower oil and dry whey as emulsifier. The systems were studied by Turbiscan, light scattering and confocal laser scanning microscopy. Aqueous phase may contain a 20 wt% sucrose solution or 0.3 wt% xanthan gum. Whey powder had two different protein contents 35 and 75 wt%. The 75 wt% powder had smaller droplet sizes for the same total solids. Droplet sizes did not change significantly by addition of sucrose or xanthan gum. Emulsions destabilized mainly by creaming with exception of the ones that contain 14 wt% whey proteins. Addition of both sucrose and xanthan gum increased stability. Confocal images were in agreement with the destabilization kinetics evaluated by turbiscan. Stable emulsions showed well formed droplets evenly distributed.

Controlling Fate of Emulsion-based Delivery Systems in the Gastrointestinal Tract by Nano-lamination of Lipid Droplets with Protein Layers.

T. Tokle, D.J. McClements, University of Massachusetts Amherst, Amherst, MA, USA

Multilayer emulsions containing lipid droplets coated with nano-laminated protein layers have great potential as delivery systems in foods. We investigated the behavior of primary, secondary, tertiary and quaternary emulsions containing lipid droplets coated by 1, 2, 3 or 4 layers of protein (lactoferrin and/or β -lactoglobulin) under simulated GI conditions. At pH 6.5, anionic β LG electrostatically adsorbed onto cationic LF-coated oil droplets, giving them highly negative charges. Further addition of LF increased the oil droplet charge indicating adsorption over β LG but it did not become positive, showing that some negative patches remained exposed. When a fourth layer of β LG was added, the negative charge increased again indicating adsorption over LF. All the multilayer emulsions showed droplet aggregation at pH 5 as they had low charges preventing electrostatic repulsion, but were stable at higher or lower pH values. Addition of NaCl (≤ 200 mM) did not affect emulsion stability. In a simulated small intestine model, the order of digestion of the emulsions was primary > secondary > tertiary. These systems may therefore be used to produce functional foods to delay digestibility and induce satiety or for controlled release of bioactives.

Influence of the Incorporation of Hardfats on the Microstructure and Consistency of Cocoa Butter.

Ana Paula Badan Ribeiro, Theo Guenter Kieckbusch, Helen Monise Masuchi, School of Chemical Engineering, University of Campinas, Campinas, São Paulo, Brazil

Fully hydrogenated oils, also known as hardfats, are currently employed in a limited number of applications in the food and chemical industries. The use of these compounds has been proposed for the improvement or replacement of the industrial process of fats and fat products crystallization, since they can act as modulators in the ordering process of the crystal network and as inducers of specific polymorphs, showing great potential for use in seeding processes, mainly for the production of chocolates and similar products. The purpose of this study was to evaluate the effect of the incorporation of different hardfats on the properties of consistency and microstructure of cocoa butter. Hardfats from palm kernel oil (FHPKO), palm oil (FHPO), cottonseed oil (FHCO), soybean oil (FHSO) and crambe oil (FHCrO), added to cocoa butter at concentrations of 1, 3 and 5% (w/w) were studied. A considerable increase in the hardness of cocoa butter was obtained with the addition of FHPO and FHSO, and the consistency characteristics in blends incorporated with FHCO and FHCrO were retained. The addition of FHPO, FHCO, FHSO and FHCrO contributed, in a scale depending on concentration, to a small decrease in the mean diameter of the crystals without changing the crystal morphology.

Melting and Solidification Properties of Palm-based Diacylglycerol, Palm Kernel Olein and Sunflower Oil in the Preparation of Palm-based Diacylglycerol-enriched Soft Tub Margarine.

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This study aims to deliver healthier alternatives to full fat products by incorporating diacylglycerol to fat products. Ternary mixtures containing sunflower oil (SFO), palm kernel olein (PKOL) and palm based diacylglycerol oil (POL-DAG) with certain proportions were designed using mixture design. The corresponding physical properties such as solid fat content (SFC) as well as deviation from SFC (Δ SFC) using nuclear magnetic resonance (NMR) and melting and crystallization properties using differential scanning calorimetry (DSC) were studied. Ternary phase behaviour was analyzed with isosolid diagrams. The eutectic behaviour was observed along the binary line of PKOL/POL-DAG at temperature ranges of 5-20°C. This was reflected in the lower heat of crystallization (Δ Hc) as well as higher Δ SFC for 50/50 mixture of PKOL and POL-DAG. Palm-based DAG-enriched soft tub margarine (PDAG-TM) containing SFO/PKOL/POL-DAG (35/15/50, (w/w)) was optimally formulated through analysis of multiple isosolid diagrams, and was found to have quite similar SFC profile as well as SMP but also lower saturated fatty acid as compared to the commercial soft tub margarine.

Extraction of Trans Fatty Acid Free Rice Bran Oil Using Supercritical Carbon Dioxide.

Masahiro Matsubara¹, Yasuhisa Nakato², Eiichi Kondoh¹, ¹Univ. of Yamanashi, Takeda, Yamanashi, Japan, ²KOA Electronics Co., Ltd, Anann-cho, Shimoina-gun, Nagano, Japan

Extraction of Trans Fatty Acid Free Rice Bran Oil Using Supercritical Carbon Dioxide Masahiro Matsubara¹, Yasuhisa Nakato² and Eiichi Kondoh¹ Mechanical System Engineering, University of Yamanashi, Kofu, Japan ²KOA Electronics Co., Ltd., Nisijyo 733, Anann-Cho, Simoina-Gun, Nagano, Japan Rice bran oil (RBO) is getting a crucial attention in cooking markets of U.S.A., upon a novel regulation of foods including a trans-fatty acid [1]. We studied

RBO extraction from rice bran using supercritical carbon dioxide (scCO₂). Crude RBO extracted was separated to oil and wax by centrifugation. The composition of the oil extracted with scCO₂ and filtered was compared with that of commercial oil extracted using hexane solvent. The commercial oil included trans-fatty acid about 0.4%. The contents of tocopherol and tocotrienol in the scCO₂-extracted oil were 4.4 and 2.6 times higher than those in commercial oil, respectively. It is also very interesting squalene extracted by scCO₂ only [2], which included at a concentration of 0.1%. Conventional commercial oil including trans-fatty acid does not match the novel regulation. Therefore, the scCO₂-extracted oil is most suitable as an alternative. [1] California Health & Human Services Agency, Sec.1. Chap.12.6 (commencing with Sec. 114377)[2] H.J.Kim, et al., Separation and Purification Technology, 15, 1999, 1-8

Crystallization and Application Behavior of *trans*-free Cocoa Butter Replacer Produced by Palm-based Oil.

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Cocoa butter replacers (CBRs) which have the similar mouth feeling as cocoa butter are normally produced by partially hydrogenated soybean, rapeseed or palm oil. CBRs are commonly used as coating fat without tempering. However, partial hydrogenation generates trans fatty acids during process, which cause cardiovascular diseases. It has been strictly limited by many countries. Therefore, the production of trans free CBRs become an important issue at industrial application area. Our study focuses on the crystallization and application behavior of trans free CBRs, which are produced by the fraction or interesterification of palm based oil. It contains at least 70% of POP and PPO in different ratios. Crystallization behavior of the blends is studied by DSC, pNMR, and X-ray. Application tests are done by making chocolate and stored them in a varied temperature for one month. The effect of PPO/POP ratios on crystallization, application behavior is discussed and concluded from this study.

Effect of Surface Properties of Solid or Liquid Oil Droplets on the Distribution and Reactivity of a Model Lipophilic Ingredient in Nanoemulsions.

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Bioactive lipophilic ingredients (BLI) as flavors, pigments or antimicrobials are often added to food products to produce a desired functionality. Most of these BLI are chemically labile. Therefore, there is a need to use protective strategies such as encapsulation in oil-in-water (O/W) emulsions. The objective of this work was to investigate the effect of the emulsifier type on the distribution and reactivity of a model BLI in nanoemulsions and solid lipid nanoparticles. The model compound selected was a lipophilic spin probe (4-phenyl-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl, PTMIO). Nanoscale emulsions were prepared by homogenizing n-tetradecane or n-eicosane containing PTMIO into emulsifier aqueous solutions. Emulsifiers with various physical properties were chosen, including sodium caseinate, lecithin, sodium dodecyl sulfate (SDS) or dodecyltrimethylammonium bromide (DTAB). According to the probe properties determined by electron paramagnetic resonance (EPR), the distribution of PTMIO between the different phases of nanoemulsions was assessed. In protein-stabilized emulsions, the probe molecules partitioned between aqueous and lipid environments and exhibited high mobility. In low molecular weight emulsifier-stabilized emulsions, a third population of less mobile probe molecules appeared, suggesting emulsifier-PTMIO interactions. The reactivity of PTMIO was measured after addition of water-soluble reactants and was found to be highly dependent on its location and on the droplet surface charge.

The Use of Immobilized Enzymes in Ionic Liquid Media for the Intent of Inter/Transesterification of Triglycerides.

Amro Alkhudair, Gianfranco Mazzanti, Department of Food Science, Dalhousie University, Halifax, NS, Canada

Enzymes are used for the catalysis of many reactions in the food science industry. To prevent the costly enzymes from being mixed with the product and to allow reusability, the enzymes are immobilized. Immobilization further serves to enhance the stability of the enzymes and therefore increases the catalytic activity. Organic solvents are currently the most common medium used for reactions involving immobilized enzymes. A promising new medium that might have better properties than organic solvents when using enzymes is ionic liquids. Unlike organic solvents, ionic liquids have low vapor pressure and are therefore non-volatile. Another advantage ionic liquids possess over organic solvents is their capability of forming clean aqueous biphasic systems. In this study, two types of triglycerides are subjected to an

enzymatic reaction in an ionic liquid medium and the enzymatic rate is compared to that of a similar reaction conducted in an organic solvent medium. Both reactions are then analyzed for efficacy through the success of the enzymes producing a reaction with complete esterification of the triglycerides via high pressure liquid chromatography. To further determine the better medium, several cycles will be employed and the enzyme activity for both media noted to see if there is a reduction in effectiveness.

Effect of Power Ultrasound (US) Treated Lipid on Physicochemical Qualities of Baked Products.

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Baked foods serve as one of the main staple food sources for consumers. Lipids play an important role in the quality of these products. In general, lipids contribute to several product characteristics such as tenderness, moist mouthfeel, air incorporation, lubricity, flavor, structure and shelf life. The objective of this research was to evaluate the effect of power ultrasound (US)-treated shortening on the physicochemical qualities of baked products such as cookies, pie crusts, and cakes. When cookies were formulated with a US-treated shortening a significantly less dense cookie dough, lower spread, higher height and a lower fracturability were observed ($p < 0.05$); while a higher percentage of shrinkage, a lower height and a lower breaking strength were obtained in pie crust formulated with US-treated shortening. Last but not least, when cakes were formulated with the insonated shortening a lower dough density and lower resistance in compression test were observed. These results suggest lipid treated with power ultrasound contributes to air incorporation during product formulation which results in a baked product with desired characteristics.

Time Resolved X-ray Diffraction Study of Trilaurin and Trimyristin Binary Mixtures under Different Cooling Rates.

Pavan Karthik Batchu, Gianfranco Mazzanti, Dalhousie University, NS, Canada

The crystallization patterns of several binary mixtures of trilaurin and trimyristin were studied using time resolved synchrotron X-ray diffraction under different cooling rates and different holding temperatures. Polymorph β' was formed at slower cooling rates and during isothermal crystallization. At higher cooling rates, unstable polymorphs (α) were often formed especially in mixtures rich in trimyristin. At the start of the crystallization process very often two different polymorphs co-existed, later the unstable polymorph was gradually transformed into a more stable polymorph. The presence of solid solutions formed by these binary mixtures was shown by small angle d-spacings within the range of pure trilaurin and trimyristin. Formation of multiple phases was evidenced by different SAXS and WAXS d-spacings in the same sample. These different solid solutions sometimes had the same polymorphic form but different composition, whereas in other cases these phases had different composition and polymorphic form. The first case was evidenced by the presence of a single WAXS pattern along with multiple SAXS patterns whereas the latter showed different SAXS and WAXS patterns for the same sample. There were two different types of β' polymorphs identified and this type depended on the composition of the sample.

Fractionation Procedures for Obtaining Cocoa Butter Equivalent from Enzymatically Interesterified High Oleic Sunflower Oil.

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Solvent free lipase catalyzed incorporation of fatty acid mixture (MFA) in high oleic sunflower oil (HOSO) by the 1,3-regiospecific lipozyme RM IM resulted in the formation of a complex mixture of triacylglycerols (TAGs) and free fatty acids. The MFA incorporation in HOSO lead to the formation of the desired cocoa butter TAGs namely distearoyl-oleoyl-glycerol (SOS), palmitoyl-oleoyl-stearoylglycerol (POS) and dipalmitoyl-oleoyl-glycerol (POP). A combination of fractionation steps involving initially the removal of free fatty acids (FFA) from the product mixture by short path distillation under vacuum, followed by fractional crystallization of the TAGs in hexane and/or acetone, gave a fat, with a TAG composition and melting profile comparable to that of cocoa butter as measured by reversed phase high performance liquid chromatography (HPLC), pulsed nuclear magnetic resonance (pNMR) and differential scanning calorimetry (DSC).

Light Stability of Two Types of Lycopene in a Five Component Microemulsion.

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Microemulsions (ME) are a well-known and studied field, having applications in many industrial technologies. The ability to mix oil and water to a stable mixture and to solubilize different types of active ingredients for different purposes has made this field a matter of interest for many researchers. Lycopene is a lipophilic natural pigment that has great importance to the food industry. It is used as a food coloring agent due to its non-toxicity feature. It is light sensitive to oxidative degradation by visible light radiation which limits its shelf life. In this study we investigated the stability of two different types of Lycopene: pure and oleoresin Lycopene, both solubilized in ME and dissolved in organic solvent. Concentration of Lycopene was measured during two months in order to determine the percent of Lycopene remained after its exposure to daylight. The results show that oleoresin Lycopene maintains its concentration throughout the whole period, in both systems (ME and in solvent). On the contrary, pure Lycopene decreases up to about 50% of its initial concentration during the first week, also in both systems. These results indicate the important role of oleoresin in the Lycopene preserving mechanism and the possibility that ME does not affect its stability. The mechanistic aspects of this oxidation differences will be discussed in the presentation.

Isolation and Characterisation of Flaxseed Lignan.

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Flax seeds contain high levels of dietary fibre including lignans. The major lignan in flaxseed is secoisolariciresinol (SECO) which is present in the form of the diglucoside, i.e. SDG. SDG is an antioxidant which reduces hypercholesterolemic atherosclerosis and this effect is associated with a decrease in serum cholesterol, LDL-C, and lipid peroxidation products and an increase in HDL-C and antioxidant reserve. Lignans are generally dimers containing a dibenzylbutane skeleton. Even though there appears to be significant commercial uses for SDG in foods and medicines, the greatest problem is that they are still only laboratory curiosities because they are available in only very small quantities in flax seeds. In the present study, method was developed to extract lignans from de-oiled flax seeds. The de-oiled meal was treated with acetone/water to extract the lignans. The lignan-rich solvent was then concentrated in rotary evaporator. The concentrate obtained was subjected to a base-catalysed hydrolysis separate the cyanogenic glycosides from SDG followed by a liquid-liquid extraction with ethyl acetate/water to isolate pure SDG. The presence of SDG in the extract was confirmed by high performance liquid chromatography (HPLC). The product will be further characterised by ^{13}C NMR and yield will be calculated by preparative HPLC.

Effect of Pickled Process on Antioxidant Activity of Bioactive Compounds of Jalapeño Pepper (*Capsicum annuum* L.).

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Hot peppers (*Capsicum annuum*) are widely produced and consumed in many countries as raw, cooked, or processed products. Among the most consumed hot peppers jalapeño is reported, which is commonly consumed in pickled form. Pickled process involves conditions (pH below 4 and temperatures of 80-90°C) that may cause a marked loss of different bioactive compounds. For this reason, the aim of this study was evaluate the effect of pickled process on the composition and antioxidant activity of phenols, flavonoids, carotenoids and tocopherols in pickled Jalapeño pepper. The results showed a reduction of 30.86 and 17.79% of phenols and total flavonoids after the process, respectively. The antioxidant activity of phenolic fraction was not reduced (ABTS•+); however, antioxidant activity of lipid fraction (carotenoids and tocopherols) was reduced 23.52% by the process. Among tocopherols only α -tocopherol was found, which was not reduced by the process. Total carotenoids reduction was 42.9%. In fresh pepper, lutein, chlorophyll-a, chlorophyll-b and β -carotene were found; which chlorophyll-b was not detected after process. Pickled process of jalapeño pepper had an effect slightly negative on the bioactive compounds and antioxidant activity in lipid fraction.

Viscous Heating in a Mini-Couette Cell Used in Rheo-XRD and Rheo-NMR Research with a Non-Newtonian Standard Fluid.

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A mathematical model is proposed to describe the temperature increase due to viscous heating in a mini-Couette cell used in Rheo-XRD and Rheo-NMR experiments on crystallization of triglycerides. The model was tested using standard non-Newtonian rheological oil, NIST standard reference material (SRM) 2490. The model is firstly developed based on the viscosity pattern of the material as a function of temperature and shear rate at low shear rates, to derive the non-dimensional temperature and non-dimensional velocity of the shear, and their derivatives. Numerical solutions of the four variables are found to satisfy the boundary conditions of the mini-Couette cell. The temperature and viscosity behaviour of the material is then analyzed under high shear rate, to study the viscous heating effect of the oil, and to test the model. The model developed in this work is essential for the interpretation of viscometric experiments of non-Newtonian materials done under shear flow in small-enclosed cells with high curvature. It also helps with the understanding of the crystallization behaviour of mixtures of triglycerides, and with the calibration of the rheometer under high shear rate conditions, as well as for the design of industrial shearing crystallizers.