

2011 Annual Meeting Abstracts

Food Structure & Functionality Forum

MONDAY

MORNING

FS&FF 1: Food-Body Interactions

Chair(s): I. Appleqvist, CSIRO, Food and Nutritional Sciences, Australia; and M. Paques, Royal FrieslandCampina, The Netherlands

Chewing Simulator for Food Texture Studies. R. DeLong, L. Lin, Y. Heo, A. Fok, W. Douglas, University of Minnesota School of Dentistry, Minneapolis, MN, USA

A central pattern generator controls human chewing. The base pattern is mediated by peripheral sensors in muscles and periodontal ligaments reacting to food texture. Objective: Develop a chewing simulator controlled by food texture to understand the role of chewing in texture perception. Methods: Two linear motors provide motion: one mounted 15 degrees from vertical; the second mounted at a right angle to, and carried by, the first. Because the human sagittal plane chewing path is nearly linear, realistic chewing motion is achieved. A load cell, mounted above the motors, measures force. Control is provided by calculating the change in load per unit time and expected maximum load. If the load is greater (smaller) than that required to fracture the food, the load rate is decreased (increased); thus, food properties modify the base pattern control. As a first test of the system, response time and paths of motion were calculated using soft and hard "food" materials. Results: The soft and hard load rates were 26.3 N/s (loading time: 0.4s) and 229.0 N/s (loading time: 0.05s); and the response times were 0.018s and 0.019s, respectively. Paths of motion visually matched human motion. Conclusions: The average system response rate (0.0185s) is similar to that measured for humans (0.023s) as is the 3D motion; therefore, the system, as designed, is capable of responding to changes in load rate mediated by food texture.

Gelatin-based Emulsion Gels for Drug Release. G. Thakur², M.A. Naqvi¹, D. Rousseau¹,
¹Ryerson University, Toronto, Ontario, Canada, ²Indian Institute of Technology, Kharagpur, West Bengal, India

Food-grade emulsion gels consisting of indomethacin-loaded vegetable oil droplets finely dispersed within genipin-crosslinked gelatin-based hydrogels were characterized for their physical and drug release properties. Varying the weight ratio of the gelatin and oil phases between 5:1 and 5:5 was used to modulate construct swelling and drug release. The dispersed oil droplets generally became larger, more polydispersed and aggregated with an increase in oil fraction. Crosslinking with genipin increased the puncture strength of the gels vs. their uncrosslinked counterparts and was necessary to prevent breakdown. Swelling of the emulsion gels, which was strictly dependent on the proportion of gelatin, demonstrated Fickian behaviour at all gelatin:oil ratios. Indomethacin release followed Fickian diffusion at higher oil fractions

only, demonstrating coupled Fickian and Super-Case II transport at lower oil ratios (5:1, 5:2 and 5:3). These results showed that crosslinked emulsion gels are a viable tool for drug or bioactive release.

Salt Taste Intensity in Water-in-Oil Emulsion Systems. M. Rietberg¹, D. Rousseau², M. Marcone¹, L. Duizer¹, ¹University of Guelph, Guelph, Ontario, Canada, ²Ryerson University, Toronto, Ontario, Canada

There is a push to develop reduced-sodium products that are appealing to consumers. This research investigates liquid foods, with a water-in-oil (W/O) emulsion as the salt (NaCl) delivery vehicle. Polyglycerol Polyricinoleate (PgPr) concentration, NaCl content, and dispersed phase fraction were varied to examine how these factors contribute to the perception of salt. The most significant factor was the aqueous phase fraction of the emulsions; increasing the mass fraction of the aqueous phase was significantly correlated with increased salt taste intensity (P

AFTERNOON

FS&FF 2: Phase Transitions: Engineering and Stability

Chair(s): S. Martini, Utah State University, USA; and D. Rousseau, Ryerson University, Canada

Studies on Interaction of Milk Casein and Ovalbumin in the Presence of Fatty Acid Salts.

Naoko Yuno-Ohta, Motomi Sawaki, Mari Endo, Junior College at Mishima of Nihon University, Mishima, Shizuoka, Japan

We have reported on the formation of fatty acid salts (FAS) induced gel from β -lactoglobulin (β -LG) and β -casein (β -CN) in last conference. FAS has no effect on the gelation of casein whereas it easily induced gel formation of β -LG at ambient temperature. On the other hand, FAS induced a gel from the mixed system containing β -CN and β -LG. In this study, using rheological measurements, electron microscopy and FT-IR analysis, we investigated the interaction of two types of casein (α -CN, β -CN) and OVA which easily turns to molten globule-like state in the presence of FAS. We found that although 5% CN fractions could form gels with 5% OVA in the presence of 0.2M sodium chloride and 2% sodium caprate, two CN gels were different in rheological properties, particle size in SEM observation and changes in intermolecular β -sheet in FT-IR analysis. Namely, β -CN and OVA mixture formed more viscoelastic gel composed from smaller particles of denatured proteins containing more intermolecular β -sheet than that of α -CN and OVA mixture. The different behaviors may be due to the difference of protein hydrophobicity between two CN fractions.

The Structure of Solid Nanoplatelets in Molecular Fluids: Theoretical Models and Computer Simulation.

D.A. Pink¹, B.E. Quinn¹, F. Peyronel², N. Acevedo², A. Marangoni², ¹St. Francis Xavier University, Antigonish, NS, Canada, ²University of Guelph, Guelph, ON, Canada

Experiments [N.Acevedo & A.Marangoni 2010 Crys.Growth Des. **10**, 3327, D.Tang & A.Marangoni 2008 J.Coll.Interface Sci. **318**, 202] have shown that the solid triacylglyceride

components in triacylglyceride fluids exhibit fractal arrangements. However, a number of questions, of relevance to practical applications, raise themselves. (i) is the structure observed in thermal equilibrium and, if so, over what time-scale? (ii) can one relate the strength and anisotropy of the interaction between platelets to the larger-scale structure exhibited by the platelets? specifically: what is the relationship between fractal dimension and the interaction strength and anisotropy? We have modeled such a system and investigated the structures which emerge if one assumes the system to be dominated by diffusion-limited aggregation (DLA). We developed a coarse-grained model of the platelets, identified the interactions between the platelets, used computer simulation in order to bring about aggregation and analyzed the structure using structure functions.

Microstructure and Rheology of Butter: Effects of Cream Temperature Treatment. Stine Rønholt, Thomas B. Pedersen, Kell Mortensen, Jes C. Knudsen, University of Copenhagen, Faculty of Life Sciences, Rolighedsvej 30, 1958 Frederiksberg C, Denmark

Material and rheological properties of crys-tallized fat are of importance within a range of foods and personal care products. We show that simple temperature treatment of cream, applied prior to preparation of butter, was useful to control rheological properties and distribution of water in butter. Microstructural features that may influence macroscopic properties of butter were furthermore identified. Four cream treatments were selected: Cooling rates at 8.5oC/min (fast rate) and 0.3oC/min (slow rate) and two maturation procedures 48 and 120 hours at 5oC. Confocal laser scanning microscopy revealed that butter prepared from slow and fast cooled cream contained micrometer sized intact fat globules, however, a less distinct globular structure was observed in butter prepared from matured cream. Butter prepared from matured cream was softer and had about 2-fold lower elasticity compared to butter prepared from fast and slow cooled cream, shown by small and large deformation rhe-ology. The water fraction in the butter was dependent on the cream treatment and use of non-matured cream facilitated incorporation of water into the butter. The average water droplet size was somewhat smaller in butter made from matured cream compared to water droplet sizes in butter made from non-matured cream, shown by nuclear magnetic resonance.

TUESDAY

AFTERNOON

FS&FF 3: New Concepts for Food Structuring

Chair(s): G. Yang, Kellogg North America Co., USA; and TBD

Effect of Symmetric/Asymmetric Triacylglycerol Ratio on the Crystallization Behaviour and Storage Stability of Fat Blends. V. De Graef¹, J. Vereecken¹, K. Smith², K. Dewettinck¹,
¹Ghent University, Ghent, Belgium, ²Fat Science Consulting, Bedford, UK

Triacylglycerols (TAG) are the main constituents of fat-containing food products such as margarine and chocolate. The physical characteristics of the fat crystal network created by TAG monitor changes in the functional properties of these products such as their texture, plasticity and

mouth feel. Nowadays, the role of the TAG structure becomes very important due to the trend to develop more healthy fats with a reduced level of trans and saturated fatty acids. In this study the role of the place of the fatty acids on the glycerol backbone is investigated by comparing vegetable oil blends with the same saturated fat content (40%), but with a varying amount of symmetric and asymmetric TAG. Crystallization properties were investigated by pNMR and DSC and further characterized by XRD analysis. The structure development after crystallization was further monitored by pNMR, microscopy and texturometry. The results demonstrated that the blends had comparable crystallization rates but a different crystallization mechanism. For some blends an isosbestic point was observed by XRD, while for other blends an independent crystallization of α and β' crystals occurred. Moreover, symmetric TAG based blends were harder at low storage temperature, while asymmetric TAG based blends were harder at high storage temperature.

Triacylglyceride Fluids in Confined Spaces: Fluid Structures and Interactions on the Nanoscale. D.A. Pink¹, F. Peyronel², C. MacDougall¹, A. Marangoni², C. B. Hanna³, S. Razul¹,
¹St. Francis Xavier University, Antigonish, NS, Canada, ²University of Guelph, Guelph, ON, Canada, ³Boise State University, Boise, ID, USA

We have carried out computer simulations of (i) pure fluid triolein and (ii) a fluid triolein-trilaurin mix between two solid planar parallel surfaces separated by nanoscale distances, using atomic scale molecular dynamics (GROMACS). Our intent was to investigate in more detail the density oscillations and related phenomena that we reported at AOCS2010 [Pink et al. 2010 *Meanfield Theories and their Validity at the Nanoscale for Lipids*]. Here we show details of the nanoscale fluid structures and report on the phase separation that occurs in the triolein-trilaurin mix. We show that the fluid density between the solid surfaces decreases markedly when the distance, d , separating the two surfaces is less than ~ 2 nm. We outline analytical calculations which show that, in the presence of liquid density oscillations, the interaction between the two solid surfaces no longer follows the $1/d^2$ law that emerges if the liquid is assumed to be homogeneous, but contains other d -dependences.

Crystallization Behavior of Anhydrous Milk Fat and Sunflower Oil Wax Blends. R. Kerr¹, X. Tombokan², S. Ghosh², S. Martini¹, ¹Department of Nutrition, Dietetics, and Food Sciences, Utah State University, Logan, UT, USA, ²Brunker Optics Inc., The Woodlands, TX, USA

This research evaluates the effect of Sunflower Oil wax (SFOw) addition on the crystallization behavior and functional properties of Anhydrous Milk Fat (AMF). Induction times or nucleation, melting profiles, microstructure of crystals, and hardness were evaluated for samples of pure AMF, AMF with 0.1% SFOw, and AMF with 0.25% SFOw. Results from this research show that the addition of waxes induced the onset of crystallization of AMF by inducing its nucleation as evidenced by decreased induction times of nucleation and the smaller crystals obtained. Even though waxes induced the nucleation of AMF, an induction of crystal growth was observed only at low temperatures (27°C) as shown by higher enthalpy values after samples were kept for 90 min at crystallization temperature. Significantly harder lipid networks ($p < 0.05$) were observed in AMF samples crystallized with 0.25% SFOw at 27, 29, and 30°C; while significantly harder networks were obtained with the 0.1% SFOw addition at lower temperature only (27°C). This increase in the hardness of the lipid network can be explained by the smaller crystals observed

using polarized light microscopy. Results presented in this paper suggest that SFOW can be used as an additive to alter the physicochemical properties of low trans-fatty acid lipids.

Using High Intensity Ultrasound as a Tool to Change the Functional Properties of Interesterified Soybean Oil. Y. Ye, A. Wagh, S. Martini, Utah State University, Logan, UT, USA

Lipid scientists have been searching for new strategies to optimize the functional properties of healthy fats that can be used as trans-fatty acids replacements. In this research, HIU was used in a low saturated shortening to generate small crystals and therefore harder materials. Polarized light microscopy was used to detect crystal morphology, texture profile analyzer was applied to measure hardness, while a dynamic rheometer was used to study viscoelasticity (G' , G'' , and η). HIU was applied to the samples using different acoustic power levels. The higher the power level the greater the effect on crystal size reduction. The higher power setting was applied when the sample was crystallized at different temperatures. Results show a significant induction in crystallization and the generation of smaller sizes crystals as a consequence of HIU application, especially when samples are crystallized at higher temperature (32 °C). In addition, a significant increase in hardness (increase of 1 to- 3 times in sonicated samples) and viscoelasticity was also observed. Values for G' increased from 50 Pa to 1,500 Pa at 32 °C, G'' increased from 25 to 150 Pa at 32 °C and viscosity increased from 2,359 Pa·s to 40,090 Pa·s at 32 °C.

Influence of Shear and Cooling Rates on the Nano- and Micro-crystalline Morphology of Binary Mixtures of Fully Hydrogenated Soybean Oil and Soybean Oil. N. Acevedo, J. Block, A. Marangoni, University of Guelph, Guelph, ON, Canada

External shear and temperature fields have a strong effect on the crystallization behaviour of fats, and are thus important unit operations that can be used to tailor the crystalline structure and physicochemical characteristics. Blends of fully hydrogenated soybean oil in soybean oil were crystallized at different wall temperatures statically and under laminar shear rates of 25 and 300s⁻¹. Samples were characterized using Polarized Light Microscopy, Cryo-TEM, and Small-angle X-ray Diffraction. Oil-binding capacity was also evaluated. Shearing greatly affected the structure at the nano- and mesoscale. Laminar shear processing promoted the growth of spherical crystalline particles; "solid-lipid mesoparticles". At low shear rates, blends showed an increase in particle size with the increase in wall temperature at the nano- and mesoscale; however, at a shear rate of 300s⁻¹ this effect was observed only at the mesoscale. Crystallization under high shear rates led to the formation of a weak network with a low oil-binding capacity and promoted the asymmetric growth of nanoplatelets. In statically crystallized blends nanoplatelets had an aspect ratio of 2, while in sheared blends this value increased up to 5. Shear-temperature combinations were successfully used to structure fats at the nano and mesoscale.

The Crystallization and Solidification of an Edible Oil Organogel Under the Influence of Shear and Thermal Gradients. E.D. Co, A.G. Marangoni, University of Guelph, Guelph, ON, Canada

The following research examines the combined effects of thermal gradients and oscillatory shear fields on the material properties of a vegetable oil organogel structured by a Self-Assembled

Fibrillar Network (SAFiN) of 12-hydroxystearic acid (12-HSA) crystalline fibrils with a view to its technological application in foods, cosmetics and pharmaceuticals. Oscillatory shear was applied to the pro-gel solution as it was crystallized under slow/non-isothermal (1 °C/min) and fast/isothermal (approximately 30 °C/min) regimes. Gels crystallized rapidly exhibited a greater storage modulus (G') than slow-cooled gels, but the oil binding capacity was not affected significantly relative to slow cooled gels. The application of progressively greater oscillatory stresses led to a decrease in the G' of the slow-cooled gel. The application of shear did not markedly affect the viscoelastic properties of the fast-cooled samples. Microstructurally, the application of shear to the slow-cooled sample resulted in the formation of thicker fibers. In the fast-cooled gels, the addition of shear resulted in small bell-shaped spherulites.

The Role of Diffusive Path Tortuosity on Oil Migration through Cocoa Butter. Farnaz Maleky, Alejandro Marangoni, University of Guelph, Guelph, ON, Canada

The effects of laminar shear on the migration kinetics of stained triacylglycerol (TAG) oil through cocoa butter were characterized and quantified. Several models were used to study this phenomenon. A lower migration rate and a low diffusion coefficient were observed in cocoa butter crystallized under laminar shear. These samples had a smaller crystallite size indicating that particles of this size will retard oil migration. The arrangement of the crystalline component also had a strong effect on the oil migration rate. Liquid oil diffusivity was decreased in samples that exhibited alignment of the crystalline material along a given axis. Moreover, the tortuosity of the diffusive path in the sheared samples was higher than that of the static sample. Finally, the relationships between the structural factors (nanoparticle size, domain size, tortuosity and particle distribution) and the permeability coefficients suggest that shear crystallization can retard oil migration by reducing the network's permeability.

OSCAR: An Innovative Device to Measure Static Permittivities for the Quantification of Lipid Interactions. F. Peyronel^{1,4}, I. Neeson², D. Pink^{3,4}, A. Marangoni^{1,4}, ¹University of Guelph, Guelph, ON, Canada, ²VN Instruments, Elizabethtown, ON, Canada, ³St. Francis Xavier University, Antigonish, NS, Canada, ⁴Advanced Foods and Materials Network of Centres of Excellence, Canada

Interactions between fat particles can be quantified by calculating the Hamaker coefficient, A_H . Lifshitz Theory gives an equation for A_H involving permittivities at all frequencies. Under certain conditions, this can be simplified as the "working equation" involving static permittivities, $\epsilon_r(0)$, and refractive indices [J.N. Israelachvili Intermolecular and Surface Forces 1992]. To measure $\epsilon_r(0)$, we designed and built a user-friendly, inexpensive, accurate device, OSCAR, to measure the capacitance of oils or fats in the limit of zero-frequency. OSCAR can also determine the amount of polar compounds in oils and solid fats. OSCAR uses a parallel plate capacitor with guard rings and thermostatic control to measure the temperature-dependent capacitance of a cell (6.25 cm² area, 1 mm gap) filled with fats and/or oils. We apply our test voltage to the RC circuit (1000Mohms in series with the measurement cell) and integrate the current flow to obtain the charge. We wait until the current reaches a steady state value, so that the output of the instrumentation amplifier has settled down to a static value after the charge flow to the capacitor has essentially stopped. We shall discuss the operation of OSCAR, present

results of measurements of $\epsilon_r(0)$ for various oils and fats, and present results for A_H .

WEDNESDAY

MORNING

EAT 4 / FS&FF 4: Cocoa Butter and Chocolate Structuring

Chair(s): N. Widlak, ADM Cocoa, USA; and K. Dewettinck, Ghent University, Belgium

Ultrasonic Characterization of Dispersions of Sugar in Vegetable Oil. U. Yucel, J.N. Coupland, The Pennsylvania State University, University Park, PA, USA

Solid-in-oil dispersions are common in foods (e.g., liquid chocolate, flavor slurry suspensions) yet their properties are difficult to monitor, particularly online. In the present work we consider the use of ultrasonic sensors to characterize the properties of oil-continuous dispersions of sucrose. Through-transmission ultrasonic attenuation measurements (2.25 MHz) were used to monitor changes during dispersing, agglomeration, and sedimentation of sucrose crystals (8-16 wt%, $d \approx 29.8 \mu\text{m}$) suspended in vegetable oil. Following the addition of sugar into the stirred oil, ultrasonic attenuation increased instantaneously due to the presence of air pockets in and around the clusters of sucrose crystals, and then decreased back to a steady-state value proportional to sugar concentration. Next, the dispersed crystals were agglomerated by the addition of small volumes of water (0-1%). Ultrasonic attenuation increased over several minutes following the addition of water. Finally, the agglomerated crystals were allowed to sediment quiescently. Agglomeration decreased the time taken for the sucrose to sediment, but was not uniform suggesting the formation of different sized-populations of crystals. The presence of a few, very large particles was confirmed by micrometer measurements.

A Novel Approach to Measure Yield Stress in Chocolate. V. De Graef¹, F. Depypere¹, M. Minnaert², K. Dewettinck¹, ¹Ghent University, Ghent, Belgium, ²Barry Callebaut, Aalst, Belgium

In terms of rheology, liquid chocolate shows a non-Newtonian behavior that can be characterized by a yield stress and plastic viscosity. The flow behavior is influenced by processing parameters such as conching, the fat content, the amount and type of emulsifiers, the particle size distribution and tempering. In general, yield stress is determined by shear rheology experiments and the data are plotted as viscosity as a function of shear stress or shear stress as a function of shear rate. For the shear stress-shear rate plot, a frequently used approach to estimate the yield stress is to fit the data to one of several models. Even though IOCCC recommendation is not to use the Casson model, it is still frequently applied as it provides a good fit to the experimental data for the shear rate ranging from 5s⁻¹ to 60s⁻¹. However, this model is unable to resolve real differences between chocolate samples that manifest outside this region. In this study, oscillatory rheology was applied and the stress at the end of the LVR is taken as an estimate for the yield stress. As such, the yield stress could be determined without the use of mathematical models or stress values at fixed shear rates.

Influence of Cocoa Butter Refining on the Quality of Milk Chocolate. N. De Clercq¹, K. Moens¹, F. Depypere¹, J. Vila Ayala², W. De Greyt², K. Dewettinck¹, ¹Ghent University, Ghent, Belgium, ²Desmet Ballestra Group, Zaventem, Belgium

Cocoa butter was subjected to a refining process by applying a silica treatment and/or a packed column steam refining. The silica treatment of cocoa butter improves its quality by removing primary and secondary oxidation products. The steam refining primarily removes free fatty acids being the deterioration products of lypolysis. During the refining process the column temperature and the amount of silica was varied to obtain cocoa butters with a different refining quality. In the next step the cocoa butters were used in the production of a milk chocolate. DSC, rheology and texture analysis were used to investigate the effect of refining of cocoa butter on the final milk chocolate quality.

Chocolate Microstructure Influences Oil Migration Rates. D. Rousseau, M. Arduini, Ryerson University, Toronto, Ontario, Canada

The objectives of this study were to assess the effects of 3 moulding temperatures (5, 15 and 20 °C) on the microstructure, oil migration kinetics and volume of a model filled confection consisting of laboratory-tempered dark chocolate and a hazelnut oil/icing sugar filling. Significant changes in chocolate microstructure were observed based on the moulding temperature used, which also impacted oil migration kinetics. Using HPLC, triolein from hazelnut oil was used as the marker to monitor migration in relation to the 1,3-distearoyl-2-oleoylglycerol peak representing cocoa butter. Using a Fickian model, the mechanism for the migration of foreign triacylglycerols into chocolate was evaluated for 1 month. Deviations from Fickian diffusion were noted with increasing storage time, and resulted from the fat solubilization-induced breakdown of the chocolate matrix. The rate of migration and diffusion coefficient was significantly higher for the 15 °C moulded chocolate, resulting in a confectionery product with a severe loss in quality. The filled dark chocolates tempered at 20 °C showed the smallest increase in volume and most negligible deterioration over 4 weeks. Overall, the results from this study offered some insight into the optimization for the production and storage of filled chocolates.

Crystallization of Cocoa Butter. R. Campos¹, A.G. Marangoni², ¹Mars Chocolate North America, USA, ²University of Guelph, Guelph, Ontario, Canada

This investigation into cocoa butter crystallization examines the effects of extrinsic (i.e., crystallization temperature and shear) and intrinsic (i.e., molecular make-up) conditions on the crystallization process and different structural levels. The degree of undercooling -affected by storage temperature- affects how different lipid species attach to growing nuclei. Lower storage temperatures result in rapid crystallizations, neglecting other process conditions. Higher storage temperatures allow for the effects of processing conditions to become evident. Shearing of the melt during cooling results in sporadic nucleation and increased crystallization kinetics, microstructures formed by numerous small particles with higher mechanical strength and melting point. Without shear, crystallization becomes disordered: lipid species progressively attach onto growing crystals according to melting point, leading to fractional crystallization events evidenced by compositional and thermal behavior differences at various crystallization times

compared to natural cocoa butter. Specific temperature and mixing profiles steer fat crystallization in industrial applications targeting macroscopic properties. In this work we also examined the effect of small compositional changes on structural levels and functionality by adding highly saturated tristearin and highly unsaturated trilinolein. Increased concentration of saturated molecules accelerates crystallization kinetics while delaying polymorphic transformations. Conversely, highly unsaturated molecules remain liquid in the crystal network's liquid fraction, enhancing molecular mobility and accelerating polymorphic transformations.

Rheo-NMR and Synchrotron X-ray Diffraction Characterization of a Crystallizing Triglyceride Mixture. M. Li, G. Mazzanti, Dalhousie University, Halifax, NS, Canada

Shear flow affects the solid content (SC), polymorphism, and phase distribution of fats. Binary mixtures of pure Triolein and Trimyristin in a ratio of 7:3 were diluted to 60% or 40% in non-crystallizing Triolein. 40% 7L3M was cooled at 10°C/min from the melt at 60°C down to 14°C, 16°C and 18°C; 60% 7L3M was cooled to 17°C, 20°C and 23°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 that describe the dependency of viscosity on solid volume fraction, to understand the effect of orientation of the crystallites at higher shear rates. To complement the study, phase transitions during crystallization were observed by time-resolved synchrotron x-ray diffraction with the same samples under the similar conditions. The cell used had the same rheometer, temperature control and geometrical characteristics as the cell in the NMR. Shear induced a strong reduction in phase transition time and variations in phase distributions, observed in both small and wide angle X-ray diffraction.

Determination by Synchrotron X-ray Microbeam of Local Compositions in a Spherulite Made by Two Triglycerides. G. Mazzanti¹, E. Ikeda², S. Ueno², K. Sato², ¹Dalhousie University, Halifax, NS, Canada, ²Hiroshima University, Hiroshima, Japan

Predicting the crystallization path of multicomponent triglycerides is difficult due to their ability to form polymorphs and solid solutions, as well as to their usual inability to form large crystals. When a binary mixture of triglycerides crystallizes, it undergoes simultaneously a fractionation process. This makes it very difficult to relate bulk averaged measurements to crystallization phenomena at the crystallizing interface. Though we have advanced in the understanding of these processes, we still do not have proven phase diagrams and kinetic models to describe them. This becomes even more difficult for multicomponent systems. In this talk we present results of using synchrotron microbeam x-ray diffraction (Photon Factory, Tsukuba, Japan) to explore spherulites crystallised from a melt of trilaurin and trimyristin. We retrace the steps of the crystallization process as its story developed, by obtaining local diffraction patterns inside the spherulite. From them we extract local compositional information as a function of position. The history of crystallization is then compared to a model for phase diagrams of binary triglyceride mixtures proposed in the literature. It becomes apparent that the model cannot properly predict the crystallization path followed by the mixture.

Ethylcellulose Solvent Substitution Method of Preparing Heat Resistant Chocolate. T. Stortz, A.G. Marangoni, University of Guelph, Guelph, ON, Canada

The development of a heat resistant chocolate (HRC) has been a formidable task challenging researchers since the 1940's. Today we have focussed on utilizing novel structuring techniques to produce chocolate which resists deformation at temperatures above 40°C. It was hypothesized that by adding ethylcellulose solubilised in ethanol to chocolate and evaporating off the EtOH an organogel could be formed in situ with the fat phase of the chocolate. HRC was produced by mixing a 20% EC in EtOH solution with molten chocolate. The EtOH was evaporated off and the resulting chocolate was incubated at 40°C for 2hr and tested for hardness. It was found that milk chocolate with 1.9% EC had a hardness of 2646gf whereas the control chocolate was too soft to be tested. Further experiments revealed that white and dark chocolates had hardness of 3007 and 1074gf respectively. The hardness of the chocolate was dependent on chocolate type, amount of EC, and molecular weight of the EC. Addition of EC to chocolate represents a new strategy for manufacture of HRC. Future work should focus on determining the mechanism by which heat resistance is achieved in these chocolates.

Novel Utilization of Mahua (*madhuca longifolia*) Seed Fat as Cocoa Butter Replacer from the Central India Region. Bhalchandra P. Vibhute, Anand S. Kulkarni, Laxminarayan Institute of Technology, Rashtira sant Tukdoji Maharaj Nagpur University, Nagpur(M.S.),INDIA, Nagpur, Maharashtra, India

Mahua (*Madhuca longifolia* syn. *Brassica longifolia*) is the widely accepted as local name for the fat from both these species. The seed and oil potential of this tree in the country is 5.00 lakh and 1.8 lakh M. tonne. The Mahua seed found in the Central India Region contains 35% oil and 16% protein. Mahua seed belongs to the botanical families of Central India region were subjected to physico-chemical properties and lipid class determination to identify their uses for commercial exploitation such as utilization of it as a cocoa butter replacer. The physicochemical properties of fat extracted from Mahua Seed found in Central India were Color: Pale Yellow, Refractive index at 40° C:1.452 ,Specific gravity at 15°C:0.856,Iodine value :58.00,Saponification value:187 etc. It is found that the Mahua kernel fat having superior quality characteristics as compare to the Cocoa Butter. Also it is cost effective over cocoa butter. At present very little work has been carried out on commercial exploitation of these seed oils in India. The work will be a step towards it, thus generating additional revenue for the poor farmers of the Central India Region to improve their standard of living.

Impact of Deodorization on the Crystallization Properties and Solidification Behavior of Cocoa Butter. A. Lechter¹, N. Widlak¹, D. Sikorski², G. Karcher², ¹ADM Cocoa, Milwaukee, WI, USA, ²ADM Research, Decatur, IL, USA

Deodorizing cocoa butter is a common industry practice to enhance the physical properties of cocoa butter by reducing free fatty acids, reducing color and reducing flavors. However, the crystallization properties of cocoa butter which are impacted by the minor constituents removed and/or altered during the deodorization process have a significant impact on solidification behavior and functional performance of chocolates manufactured with deodorized cocoa butters. This paper will review the changes in minor lipid components, crystalline properties and

solidification behavior of cocoa butter deodorized under varying process conditions. Data on crystallization kinetics, crystallization and melting profiles, solidification rates and crystal structure will be presented in addition to standard commercial methods to measure cocoa butter quality.

AFTERNOON

FS&FF 5: Successfully Performing Interfaces

Chair(s): Y. Wang, Kraft Foods Inc., USA

Stabilization of Oil-in-Water Emulsions via Interactions between Soy Protein Isolates and Polysaccharides. T. Tran, D. Rousseau, Ryerson University, Toronto, ON, Canada

The stability of soybean protein isolate (SPI)-stabilized emulsions was investigated as a function of pH in the presence of soluble soy polysaccharide (SSPS). Oil-in-water emulsions were studied via: droplet size, creaming, microscopy, and zeta potential analysis. It was found that 0.75% SPI was the critical concentration required to stabilize 5% o/w emulsions at neutral pH. At acidic (≤ 5.0) pH, the emulsions became destabilized due to isoelectric precipitation of the SPI which lead to droplet coalescence and phase separation. To prevent this, a minimum concentration of 0.50% SSPS was required to stabilize the emulsions at these lower pH values. This was attributed to electrostatic interactions between SPI and SSPS: at $\text{pH} \leq 5.0$, SPI carries an overall positive charge while SSPS carries a negative charge. This was supported by zeta potential results, which showed neutralization (binding) of SPI by SSPS at acidic pH values.

Surfactant-triglyceride Interactions Significantly Influence Water-in-Oil Emulsion Stability. S. Ghosh, D. Rousseau, Ryerson University, Toronto, Ontario, Canada

The capacity of oil-tending surfactants such as glycerol monooleate (GMO) and sorbitan monooleate to stabilize water-in-oil emulsions strongly depends on how extensively they hydrogen bond (H-bond) with the continuous oil phase. To test this hypothesis, emulsions were prepared with 40% (w/w) water and 60% (w/w) oil. The oil phase contained different concentrations of GMO or sorbitan monooleate in either canola oil (CO) or mineral oil (MO). While all MO-based emulsions were stable, those prepared with CO completely phase-separated within a few hours of preparation, even at fairly high surfactant concentrations. IR absorbance spectra of the continuous oil phase of the emulsions revealed only intermolecular H-bonding amongst the surfactant -OH groups in MO, demonstrating exclusive solute-solute interactions. By contrast, no peak for H-bonding between -OH groups was observed in CO. Rather, excess CO ester carbonyl groups H-bonded with surfactant -OH groups, resulting in strong solute-solvent interactions. It was concluded that preferential solute-solvent H-bonding significantly reduced the availability of surfactants at the water/oil interface in CO emulsions which led to their destabilization.

Role of Salt on Water-in-Oil Emulsion Stability. S. Ghosh¹, M.F. Robert², D. Rousseau¹,
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We show that water-in-oil (W/O) emulsion stability is influenced by the presence of salt in the dispersed aqueous phase. W/O emulsions containing 40% (w/w) water (with or without 5 % w/w salt) and an oil phase consisting of either canola oil (CO) or mineral oil (MO) and emulsifier were prepared by high pressure homogenization. The effect of two surfactants, polyglycerol polyricinoleate (PGPR) and sorbitan monooleate, was studied and emulsion stability was determined by sedimentation, droplet size and microscopy for 5 weeks. With MO, improved stability was observed with added salt in both sorbitan monooleate and PGPR-stabilized emulsions. Divergent behavior was seen with CO, as sorbitan monooleate-stabilized emulsions were not stable (irrespective of the presence of salt) and there was no beneficial effect in PGPR-stabilized systems. It is proposed that the presence of salt in the aqueous phase of MO emulsions improved surfactant adsorption to the interface and thus stability. In CO emulsions, preferential hydrogen bonding of the emulsifiers with the vegetable oil triglycerides reduced their availability to stabilize the water/oil interface, leading to emulsion destabilization.

Partial Coalescence of Emulsions as a Result of Partially and Totally Wetted Solid

Particles. A.B. Pawar^{1,2}, P.T. Spicer², R. Ergun¹, R. Hartel¹, ¹Department of Food Science, University of Wisconsin Madison, Madison, Wisconsin, USA, ²Procter and Gamble Co., Cincinnati, OH, USA

The phenomenon of partial coalescence is a critical component of microstructure in various food products and is a function of multiple physicochemical factors. Historically, the role of solid particles in partial coalescence has been studied using bulk measures like rheology or microscopic observations of droplet structures after the coalescence events have occurred. Here, we develop a microcapillary technique that enables physical characterization of single droplets containing colloidal particles and their binary coalescence behavior as it occurs. We explore and map the partial coalescence phenomena relative to colloidal particle adsorption behavior in emulsions. We find partial coalescence occurs for droplets with colloids adsorbed on their surface as well as for droplets with colloids partitioned internally. Using both single droplet and bulk emulsion studies, we map the droplet coalescence behavior for both systems as a function of particle volume and surface fraction in the coalescing droplets. A physical model is provided explaining the observed regimes in terms of colloidal phase behavior, rheology, and geometrical packing of particles. Exploring the regimes of partial coalescence in both systems helps us to anticipate the details of the partial coalescence phenomena occurring in the bulk scale production of food products.

Novel Carotenoid Formulation as Oversaturated Oily Solutions for Carotenoid Delivery at Minimum Process Complexity in Nutritional Product Manufacturing and Fish Feed

Pigmentation. T. Gottschalk¹, P. van Hoogevest², H. Bohn¹, M. Leigh², R. Engel¹, H. Schwebel², B. Weigl¹, ¹BASF SE, Ludwigshafen, Germany, ²Phares AG, Muttenz, Switzerland

Carotenoids are micronutrients, and positive health effects are associated with intake of these substances. Their coloristic properties are sought after in applications from beverage production to fish pigmentation. However, their exceedingly low thermodynamic solubilities in both water and oil impose a challenge on formulation technology. This contribution reports on strategies to

render carotenoids applicable for human and animal nutrition. One strategy is to prepare fine dispersions of carotenoid particles in water. These dispersions are ideal for coloration of beverages and can provide for optimized carotenoid bioavailability. Emphasis of this contribution lies on a completely new formulation technology for astaxanthin. This novel, continuous process can be integrated in the production process of fish feed. The new technology allows for the production of oily carotenoid solutions, which are highly oversaturated, yet stable over extended periods of time. The contribution focuses on the physical chemistry of the novel carotenoid delivery strategy, especially on its most challenging aspect of obtaining high oversaturation in oil without the need for solubilizing additives.

Food Structure & Functionality Forum Posters

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Effect of Aqueous Phase Composition on Stability of Sodium Caseinate Emulsions.

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The term 'stability' refers to the ability of an emulsion to resist changes in its properties over time. The development of an effective strategy to prevent undesirable changes in the properties of a particular food emulsion depends on the dominant physicochemical mechanism(s) responsible for the changes. It is therefore important for food scientists to identify the relative importance of each mechanism, the relationship between them, and the factors that influence them, so that effective means of controlling the stability of emulsions can be established. Stability of emulsions formulated with sodium caseinate as stabilizer, sunflower oil and aqueous phases that may contain sucrose, xanthan or locust bean gums were analyzed by using a Turbiscan. The mechanism of destabilization as well as the kinetics of creaming or flocculation depended on the aqueous phase composition and sodium caseinate concentration. Other factors such as viscosity, interactions with the protein, emulsion structure, oil droplet size, and processing parameters were also relevant to stability. The most stable emulsions contained 5% sodium caseinate and 20% sucrose and were prepared using ultrasound treatment. This formulation remained unchanged for at least one week.

Lemon Oil Solubilization in Mixed Surfactant Solutions: Rationalizing Microemulsion and Nanoemulsion Formation.

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Lipophilic functional ingredients are usually incorporated into aqueous-based foods and beverages in the form of colloidal dispersions. In this study, we investigated the rate and extent of solubilization of emulsified lemon oil in mixed non-ionic surfactant solutions: sucrose monopalmitate (SMP) and/or Tween 80 (T80). The influence of surfactant concentration, type,

and mixing ratio on lemon oil solubilization was investigated, with the aim of identifying suitable conditions for preparing stable microemulsions and nanoemulsions. Lemon oil solubilization was monitored by measuring changes in light scattering of lemon oil droplets after they were dispersed in surfactant solutions at pH 7. The kinetics and solubilization capacity (C_{sat}) were strongly dependent on surfactant concentration and type. The solubilization kinetics and capacity increased with surfactant concentration. The solubilization kinetics was rapid (< few minutes), with the rate increasing with increasing surfactant concentration. The value of C_{sat} increased with increasing surfactant concentration and was higher for SMP than for Tween 80 due to their different molecular geometries. This study provides important information for the rational design of food grade colloidal delivery systems for encapsulating and delivering functional lipids for food and beverage applications.

Effect of Five Fats Sources on the Physicochemical Quality of Baked Goods.

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Lipids perform multiple functions in baked goods, such as trapping air for leavening, limiting gluten development, and interfering with starch gelatinization. To achieve maximum product quality, it is important to select a lipid with an appropriate physicochemical profile. The objective of this research was to examine the relationship between the physicochemical properties of five fats (butter, lard, margarine, shortenings and vegetable oil) and the characteristics of baked goods. For both cookies and pie crusts, an inverse relationship was observed between height and the melting onset and melting point of the lipid source. A positive relationship was seen for both products with the viscoelastic moduli and hardness of the lipid source. Melting point of the fat was inversely related to the water activity and moisture content of cakes after one week of storage. In addition, a more dense cake was obtained when softer lipids were used.

Ultrasonic Characterization of Mixing and Sedimentation in Unimodal and Bimodal Sucrose-in-Oil Dispersions.

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Mixing and sedimentation of dispersions of particles can be monitored by ultrasonic attenuation measurements. Five commercial sucrose samples with different particle sizes and their blends were dispersed (8 wt%) in corn oil in a cylindrical tank (10.4 cm I.D., 15.0 cm height). After steady state was attained, the stirrer was stopped and the particles were allowed to sediment quiescently. The mixing and sedimentation was monitored as changes in ultrasonic attenuation measured by a pair of ultrasonic transducers (2.25 MHz) operating in through-transmission configuration and located 5 cm from the bottom of the tank. The time required to attain steady state attenuation after the addition of sucrose into the oil decreased and the steady-state attenuation after mixing increased with increasing particle size, while total sedimentation time decreased with increasing particle size. The effects of hindered sedimentation were only observed for the fine samples as a temporary increase in ultrasonic attenuation following the steady state sedimentation region. The total sedimentation time in the dispersions of binary mixtures decreased about to about half that of the fine fraction by itself due to the co-sedimentation of fine particles with faster-moving coarse particles.

Low Fat Mayonnaise Formulations Prepared Using Microfluidized Nano Cellulose Fibers.
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University, Ankara, Turkey

The objective of this study was to develop low-fat (LF) mayonnaise formulations containing microfluidized nano cellulose fibers as functional ingredients. Citrus nano fibers and wheat bran nano fibers were prepared using microfluidization and used as water holding agents and fat replacers to formulate low fat mayonnaise. The fat content in low fat mayonnaise was reduced up to 50% compared to full-fat mayonnaise, and the products still maintained ideal flow properties. Flow and viscoelastic parameters showed that citrus and wheat bran nano fibers added emulsions were able to form structures similar commercial mayonnaise. Stability studies using Lumisizer instrument indicated that nano fiber added low fat mayonnaise samples had much stronger emulsion stability. This study outlines methodologies for nano fiber production and utilization of them in oil-water emulsions such as mayonnaise.