FS&FF 1: Phase Transitions—Engineering and Stability

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Tocopherol and Lecithin for Edible Oleogels. Costas Nikiforidis, Top Institute Food & Nutrition and Wageningen University, Netherlands.

The texture of many food products like margarines, pastry dough, sausages etc., is achieved by including a crystallizing triacylglycerol fraction in the lipid phase of the product. This crystalline network contains considerable amounts of saturated fatty acids, which intake has been demonstrated to raise blood cholesterol and the risk of the occurrence of cardio-vascular diseases. Therefore, the decrease of saturated fatty acids in the crystalline network would be desirable. This is not a straightforward exercise, and therefore novel alternatives for oil structuring have to be generated.

According to our findings the gelation of edible oils can be achieved by adding a mixture of tocopherol and lecithin at concentrations from 5 to 20% w/w. The two components individually cannot structure oil, but their mixture, depending on the concentration, can lead to viscous pourable solutions or to non-pourable gel-like structures. The synergistic effect of these two fillers was studied by varying their ratio and their concentration. The properties of the oleogels were evaluated using microscopy techniques, texture analysis, differential scanning calorimetry (DSC), and nuclear magnetic resonance (NMR). The obtained gels were shear-sensitive and the network formation was disrupted when the temperature was higher than 35°C, but upon cooling they regain their firmness. Moreover, the addition of small amounts of water led to a change in the microstructure of the needle-like crystals and enhanced their rheological properties.

Heat-induced Gel from Lysozyme and Ovomucoid Mixture. Naoko Yuno-Ohta1 and Youko Kimura2, 1Nihon University, Japan; 2Junior College at Mishima, Nihon University, Japan.

It is known that Ovomucoid (OM) in egg white is a heat stable protein. We investigated the interaction of lysozyme (LZM) and OM using ultrasound spectroscopy (US) under heating which is followed by cooling treatment, and scanning electron microscopy (SEM) etc.

The phase transition temperature of diluted LZM solution shifted to the higher temperature by the addition of OM. Although 10% OM alone did not formed a gel, a mixture of LZM and OM in suitable proportions formed a gel almost comparable to LZM gel. However the ultrasonic attenuation increments during heat treatment for mixed proteins were small and microstructures made from the denatured protein aggregates were very fine networks different from LZM gel. These results implied that the mixed protein formed gels with higher proportion of hydrogen bonding than LZM gel which is mainly composed of hydrophobic interaction. It suggests that the addition of OM to LZM induced changes in intermolecular forces for the gel formation and regulates the gel properties.

Unsaturated Emulsifier-mediated Modification of a Model Edible Fat Crystallized Under Shear. Nuria Acevedo1, Jane Block2, and Alejandro Marangoni1, 1Iowa State University, USA; 2Santa Catarina Federal University, Brazil; 3University of Guelph, Canada.

The effects of processing using a scraped surface heat exchanger (SSHE) before and after adding unsaturated monoglyceride (UM) on blends of Fully Hydrogenated Soybean Oil (FHSO) and Soybean Oil (SO) was studied. Mixtures of 40:60 and 45:55 FHSO:SO were melted at 80°C for 30 min and crystallized statically or in the SSHE (shear rate of 25s-1) at a cooling rate of 9°C/min. Upon shearing and UM addition, polymorphic transformations towards more (beta) or less (beta prime) stable forms was governed by the combination between system concentration, composition and crystallization conditions, as determined by differential scanning calorimetry and powder X-ray diffraction. Nuclear magnetic resonance was used to measure the solid fat content (SFC) development which showed to increase with processing conditions due to the high nucleation rate induced. Processing conditions greatly affected the nano- and micro-crystalline structures which were characterized by Polarized Light Microscopy (PLM), Cryogenic Transmission Electron Microscopy (Cryo- TEM) and Scherrer Analysis of the powder X-ray diffraction data. Crystallization under shear promoted the longitudinal growth of the nano-platelets; nevertheless meso structural elements showed a decrease in their dimension under the same crystallization conditions. The relative oil loss
determined gravimetrically was inversely related to the elastic modulus and yield stress of the sheared fat blends which values were closer to the desirable usability ranges for bakery applications. Our results suggest that fully hydrogenated fats can be functionalized by crystallization in a SSHE and/or by judicious addition of an unsaturated emulsifier.

Nature and Dynamics of the Phase Transition of Monoglyceride-water System: Re-investigate. Fan Wang and Alejandro Marangoni, University of Guelph, Canada.

The monoglyceride (MG) α-gel to coagel phase transition has been discussed in the literature, and it has been suggested that such phase transition causes the release of water from the system. This current study revisits a monoglyceride-water system with MG concentrations lower than 20% (w/w) in order to gain a better understanding of the nature and dynamics of the phase transition in this system. Powder X-ray diffraction, coagel indexes from differential scanning calorimetry, optical microscopy, and rheology measurements were used to probe this phase transition. The phase behaviour and microcrystalline structure of the MG-water system shows a temperature and concentration dependence over time. This study also suggests that the water release of the MG-water system is caused by both the α-gel to coagel phase transition, and a change in micro-structure. Whether the phase transition and the change in molecular packing are independent from each other needs to be further investigated. This study is aimed at increasing the stability and shelf life of monoglyceride based products such as low fat shortenings alternatives and green cosmetics.

Factors Governing Stability and Texture of Milk Fat Based Products Produced at Industrial Scale. Stine Rønholt1, Klaus Hoeyer2, Jacob Kirkensgaard3, Kell Mortensen1, and Jes Knudsen1, 1University of Copenhagen, Denmark; 2SPX Flow Technology Copenhagen A/S, Denmark.

Development of new milk fat based products may be advanced from a fundamental understanding of the physical and chemical properties of single fat crystals as well as their interactions in a network. In the present study, milk fat based products are produced by using a scraped surface heat exchanger. Sustainable and more efficient refrigerants, such as CO2, are now introduced in industrial equipment, which allows an increase of 40 % in capacity compared to conventional use of NH3. This change in cooling rate and shear during processing is evaluated in relation to textural behavior, the underlying fat crystallization process and the effect on water droplets size. First, the fatty acid composition of the solid fat is determined using an enzymatic essay. Second, the physical properties of the fat crystal network are studied in detail at several length scales by combining rheology, 1H-NMR and 3D confocal laser scanning microscopy. Third, single crystals and crystallization are characterized by combining X-ray diffraction with differential scanning calorimetry. Our data shows, that for samples having similar fatty acid composition, a high cooling rate increased the hardness and altered the microstructure of the products, without affecting crystal polymorphism. Furthermore, the degree of working significantly affected product behaviour.

The Level of Shear During Crystallization of Milk Fat/Rapeseed Oil is Important for Final Texture. Lars Wiking1, Niels Kaufmann1, and Ulf Andersen2, 1Aarhus University, Denmark; 2Arla Foods, Denmark.

The effect of shear on crystallization, polymorphic and rheological behavior of milk fat (AMF) blended with rapeseed oil (RO) was studied. Low, medium and high shear rates were applied during early crystallization. Monitoring the further development of the complex modulus |G*| revealed that the firmest and most rapidly formed network was achieved when a medium shear was applied. Up to 20 % RO could be added without lowering the final |G*|. A similar effect was not obtained at low or high shear rates. Polymorphic behavior was studied by NMR. Both high shear and increasing amounts of RO accelerated the polymorphic transition. Shear applied in 20-30 % blends caused only 2L packing to form, while AMF and statically crystallized blends also formed 3L structures. Crystal size decreased upon increasing shear rate while solid fat content and final amount of β’ crystals were unaffected. In conclusion, applying medium shear produces a strong crystal network while high shear breaks down the microstructure to the extent which cannot be rebuild during subsequent crystallization, resulting in lower |G*|. The study emphasizes the importance of shear as a tool to tailor the microstructure and crystallization kinetics to achieve the desired texture in fat crystal networks.
Granular Crystal Formation Mechanisms in Plastic Fats. Zong Meng\textsuperscript{1}, Yuanfa Liu\textsuperscript{2}, and Xingguo Wang\textsuperscript{2}, \textsuperscript{1}School of Food Science and Technology, Jiangnan University, China; \textsuperscript{2}Jiangnan University, China.

Beef tallow (BT) and Palm oil (PO) are extensively used in the bakery shortening and margarine manufacturing ascribable its advantageous properties, such as (i) high thermal and oxidative stability, (ii) good plasticity at room temperature, etc. However, the use of BT or PO for solid fats in plastic fat products has encountered serious structural defects, the formation of granular crystals, which impair the consistency and plasticity of fat products. Thus, the understanding and control of granular crystal formation in plastic fats are very important points in the fat industry. In the present study, all BT-based and all PO-based model shortenings prepared on a laboratory scale, respectively, denoted BTMS and POMS, were stored under temperature fluctuation cycles of 5–20°C until granular crystals were observed. The lipid composition, thermal, polymorphic and isothermal crystallization behavior of the granular crystals and their surrounding materials separated from BTMS and POMS, respectively, were evaluated. The changes of nanostructure including the aggregation of high-melting triacylglycerols and polymorphic transformation from $\beta'$ form of double chain length structures to complicated crystal structures, in which the $\beta$ and $\beta'$ form crystals of triple and double chain length structures simultaneously coexist, had occurred in granular crystals compared with surrounding materials, whether in BTMS or in POMS. Accompanyingly, a slower crystallization rate appeared in granular crystal parts of both model shortenings noted above, which would yield larger and fewer numerous crystals indicated by the Avrami model analysis, and further aggregate to form large granular crystals.

Cavity Formation in High Solids Fat Crystal Networks. Robert Lencki and Richard Craven, University of Guelph, Canada.

Proper tempering is essential for producing smooth, dense and bloom-stable chocolate, but it is not entirely clear why this is the case. We have shown that under certain crystallization conditions, at high solids concentrations $\beta$-tending triacylglycerols can form gas-filled cavities within the crystal network, significantly decreasing fat density. Pulse NMR and dilatometry were used to show that cavity formation is due to the density decrease resulting from liquid-to-solid phase transitions within the fat crystal network. This leads to areas of reduced pressure that produce air pockets either via cavitation or convective transfer from the solid surface. This negative pressure effect appears to play an important role in the final microscopic structure of complex TAG mixtures such as cocoa butter. Well-tempered cocoa butter has a relatively smooth surface, higher macroscopic density, and a closed-pore void structure. In contrast, over-tempered samples were rougher, less dense, and contained large continuous gas-filled pores. Under-tempered cocoa butter had properties between these two treatments, with a continuous, yet very fine pore structure. Evidently, negative pressure phenomena have a very significant influence on how a chocolate sample de-molds, its final surface gloss, and its ability to inhibit oil migration during storage.