FUNCTIONALITY OF FAT IN OIL DISPERSIONS FOR USE AS MEAT MARINADES

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Abstract— In oil-based marinades, uniform suspension of particulates such as salt or spices requires a gel-like behavior of the matrix to prevent gravitationally driven separation (i.e. sedimentation). This can be achieved by adding an organogelator (solid fat) to liquid oil that converts the liquid oil into a solid fat-oil gel. In this study, different fat types were used as organogelator and the influence of their addition to a liquid oil on the physicochemical properties of the resulting oil-fat-dispersions assessed. Three higher melting fats and a lower melting palm fat were used. Addition of lower melting palm fat to raps oil led to formation of gels with a nearly transparent appearence. Gels were strong with high elastic (G') and loss moduli (G") but destabilized at low temperatures. Oil-fat-dispersions that contained high melting fats had a higher temperature stability but were substantially more opaque. Gels were mechanically weaker than those formed from low melting fats and thus were not able to keep spices suspended for prolonged storage periods. All oil-fat-mixtures exhibited a shear-thinning behavior.

Index Terms-oilgel, oil-fat-dispersion, fat, gelation, marinades

I. INTRODUCTION

A very common and increasingly popular way of flavoring meat is by marinating them with spice/salt mixes (McEvoy, 2003). From a physical point of view, marinades may be simply dry powdered spice mixes that are rubbed into the surface of meats (so called dry rubs), or systems in which the spices are dispersed in a liquid phase. In the latter case, the liquid phase may consist of either water or oil. Oil based systems have shown to be particularly well suited for meat products that are grilled, since surface temperatures rise more quickly than in water based systems. In addition, such systems are able to carry lipid soluble flavors or dyes such as paprika essence in the liquid oil (Vintiloiu and Leroux, 2008). However, it is difficult to disperse the spices and salt evenly throughout the liquid and the particulates tend to gravitationally separate quickly. In contrast, in water-based systems, hydrocolloids may be added to increase the viscosity of the continuous phase thereby stabilizing the dispersed spices. Thus, in oil-based marinades, an organogelator needs to be added that converts the liquid oil into a more or less solid gel (DeMan and Beers, 1987). This is typically achieved by dispersing fat crystals in the liquid oil. As a result of the interaction of the dispersed solid fat crystals in the matrix, a three dimensional fat crystal network is formed (Hughes, Marangoni, Wright, Rogers and Rush, 2009). The mechanical properties of the organogel are such that spices and even salt may be kept in suspension over long periods. Interestingly, although much is known about the structure of highly concentrated fat crystal networks (Narine and Marangoni, 1999), much less is known about fat crystal networks that contain low concentration of solid fat (< 10 wt%). In particular, little is known about the impact of fat type on the appearance and mechanical properties of the resulting gel. Therefore the objective of this paper was to investigate the physicochemical properties of fat-oil gels prepared with different fat types at a solid fat concentration of 4.5wt%.

II. MATERIALS AND METHODS

Materials. As organogelators, four different fats were used. Hydrogenated palm fat (Sett® P55) and hydrogenated vegetable fat (Sett® S69) were kindly donated by Cognis (Monheim, Germany), with melting temperatures of 55-60°C and 65-69°C respectively. Hydrogenated sunflower and hydrogenated rapeseed oil was donated by ADM (Hamburg, Germany), with melting temperatures of about 68-74°C, were used. As the liquid phase, a rapeseed oil was obtained from Bunge (Mannheim, Germany).

Preparation of Oil-Fat-Dispersions. Oil-fat-dispersions were prepared by melting a mixture of palm fat and rapeseed oil at a mixing ratio of 1:2 at a temperature of 80°C. The hot melt was then dispersed in 5°C cold rapeseed oil using a rotor-stator colloid mill system. The colloid mill was fully evacuated using a vacuum pump to prevent dispersion of air bubbles in the oil-fat network. The oil-fat-mixture was sheared in the colloid mill for 7 min at 3000 rpm with a gap setting of 50 and 350 μ m, respectively. During the 7 minute dispersion time, temperature of the oil-fat-mixtures increased from 5 to 27-33°C. All samples were prepared with 4.5 wt% solid fat and were stored for 2 days at 20°C prior to physical property analysis.

Polarized Light Microscopy. For determination of crystal structure and size, polarized light microscopy images were taken with an axial mounted Canon Powershot G10 digital camera (Canon, Tokyo, Japan) on an Axio Scope optical

microscope.A1 (Carl Zeiss Microimaging GmbH, Göttingen, Germany). Images were processed and analyzed with Gimp 2.6.6 (GIMP Development Team, USA) and Imagej 1.43n (Wayne Rasband, National Institutes of Health, USA).

L*a*b*-Color Measurements. Color/transparancy of samples were anylyzed by colorimetry. L*, a*, b* of the CIE tristimulus color system of samples were measured with a chromameter CR-200 (Konica Minolta, Marunouichu Japan) to determine the optical properties of the samples. The chromameter was calibrated against a white calibration plate with tristimulus values: Y=93.7, x=0.3159, y=0.3321 at a D65 illumination. The samples were measured five times at different positions by direct imergence of the colorimeter probe in the sample at a sample layer thickness of 10mm against a white and black background.

Rheological Analysis. A modular compact oscillatory rheometer (MCR300, Anton Paar, Stuttgart, Germany) with application software Rheoplus/32 V3.31, equipped with a plate-plate measurement system of 50 mm diameter and a gap setting of 0.5 mm, was used to perform all rheological experiments. Flow behavior was measured by increasing the shear rate of the plate plate system at 25°C logarithmically from $0.02s^{-1}$ to $100s^{-1}$. Mechanically stability of samples during heating was assessed by arecording shear stresses when samples were heated from 20°C to 80°C and sheared at a shear rate of $1s^{-1}$.

Differential Scanning Calorimetry (DSC). The melting behavior of oil-fat-dispersions was recorded using a Perkin Elmer DSC 8500 (Perkin Elmer, CT, USA). 10-20 mg of the sample was placed in a 20 μ l aluminum pan. Pans were sealed, inserted in the DSC and heated from 10 to 80°C at a rate of 20°C/min. Enthalpy of melting was calculated by integration of the heat flow rate during the phase transition.

III. RESULTS AND DISCUSSION

Results showed that fat type significantly impacted all physical properties of oil-fat dispersions, including color, rheology and temperature stability. When oil-fat dispersions were analyzed under the polarized light microscope, significant differences in fat crystal size depending on fat type were observed. The images showed that the oil-fat dispersions that had been prepared with high melting fats formed considerably smaller crystals than the oil-fat dispersion that had been manufactured with the lower melting hydrogenated palm fat (**Figure 1**). An assessment of the size indicated that crystals of the high melting fats had average particle sizes of approximately 800 - 1000nm while the lower melting hydrogenated palm fat formed crystals of $3-5 \mu$ m.

Similarly, the transparency, indicated by ΔL^* and the whiteness of the high melting fats decreased dramatically in oil-fat-dispersion that consisted of the hydrogenated palm fat, i.e. the system that consisted of the larger fat crystals (**Figure 2**). Light scattering theory suggests that maximum scattering of spherical particles dispersed in a liquid medium occurs at approximately 1 μ m (close to the average size of the palm fat crystals) and decreases again when particle become either smaller or larger (as is the case for crystallization of the higher melting fats). The difference in observed transparency and color of samples can thus be directly attributed to differences in the scattering behavior of fat crystals which governed by the size of crystals.

The rheological properties of the oil-fat-dispersions also differed substantially. Firstly, all samples exhibited a shear – thinning behavior that is, their viscosity during a continuous shear experiment continuously decreased as the shear rate increased (**Figure 3**). Figure 3 also shows that the flow curve of the oil-fat-dispersion that contained palm fat had the highest shear stress. It was also the only sample which had a slight peak in the curve, which is indicative of a plastic fat rheology. In contrast, oil-fat-dispersions with higher melting fats hat substantially lower viscosities and did not exhibit a plastic fat behavior. Moreover, the higher melting fat dispersions showed little difference in terms of steady shear rheology. Results may be due attributed to disturbances in flow fields by the presence solid fat particles. Deviations in the flow lines may cause frictional losses which increase viscosity. In addition, it appears that low melting fat crystals had an increased to flocculate, resulting in the formation of a fat crystal network with solid-like properties. The more gel like behavior of the lower melting fat dispersion was verified by dynamic rheological experiments (**Figure 4**). Measurement of G' and G' as a function of oscillation frequency showed that oil-fat-dispersions had viscoelastic properties, and exhibited at a minimum weak gel like properties. Palm fat samples had substantially higher G' and G' values suggesting that gels were mechanically stronger.

Differential scanning calorimetry and temperature scans on the rheometer both showed that the temperature stability of oil-fat-dispersions was increased when samples were prepared with the high melting solid fats. By use of these fats the melting point of the oil-fat-mixtures was increased from 45.23° C for the palm fat dispersion to more than 54° C (**Table 1**). The onset temperature of the solid to liquid transition of fats increased when high melting fats were used. The results of DSC analysis were confirmed by the rheological measurements of samples sheared at $1s^{-1}$ suring heating from 20 to 80° C. Here, viscosity of the samples decreased by more than 3 logs at a temperature of 46.1° C for oil-fat-dispersion with palm fat while sample viscosity collapsed at $56.4-58.7^{\circ}$ C in high melting fats dispersions.

IV. CONCLUSION

Results of this study showed that selection of appropriate fat types is critical in the manufacturing of functional oil-fat

based marinades. The fat type impacts not only the maximum temperature stability, but simultaneous influences other physicochemical properties such as the appearance and rheology of the dispersions. Upon cooling, higher melting fats crystallize to form smaller, but more numerous crystals. In contrast, lower melting fat form crystals in oil that are larger and less numerous. Since both mechanical behavior and appearance is a function of particle size and concentration, bit properties are subsequently affected. This behavior is thus of substantial importance to manufacturers of meat marinades. While oil-fat-dispersions are useful for the suspension of spices and salt, their stability and appearance cannot be independently regulated and thus a complete optimization of all properties is difficult. An increased temperature stability thus may come at the price of loss of transparency and a reduced ability to keep spices and salt suspended.

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TABLES AND FIGURES

 Table 1: Results of DSC melting curve of oil-fat-dispersions prepared under shear with 4.5wt% solid fat of different fat types

Fat Type	Onset (°C)	Peak (°C)	ΔH (J/g)
Palm fat	34.20 (±1.04)	45.23 (±0.15)	150.07 (±3.34)
Vegetable fat	43.52 (±0.28)	54.13 (±0.33)	169.25 (±1.15)
Sunflower fat	43.69 (±0.54)	54.04 (±0.22)	164.06 (±3.32)
Rapeseed fat	45.46 (±1.13)	54.92 (±0.86)	167.84 (±4.74)



Figure 1. Polarized light microscopy images of the oil-fat-dispersions prepared with 4.5wt% solid fat crystallized under shear; A: hydrogenated palm fat, B: hydrogenated vegetable fat, C: hydrogenated sunflower fat, D: hydrogenated rapeseed fat



80 60 Shear Stress (Pa) 40 2.0 (Pa*s) 1.5 1.0 app. 20 palm fat 0.5 vegetable fat _ sunflower fat 0.0 rapeseed fat of Fat 0 Тур 0 20 80 100 40 60 Shear Rate (s⁻¹)

Figure 2: L*-Value of oil-fat-mixtures prepared with 4.5wt% solid fat of different fat types under shear (measured against black background) and ΔL^* : difference in L*-Value measured against black respectively white background

Figure 3: Flow properties of oil-fat-mixtures prepared with 4.5wt% solid fat of different fat types under shear: flow curve at 25°C; inserted graph: $\eta_{app.}$ at a shear rate of 39s⁻¹ for the different fat types



Figure 4: (Left) Viscosity as a function of temperature of oil-fat dispersions (Right) Differential scanning calorimetry of oil-fat dispersions

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