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Studies on the Shear Stability of Partially Crystalline Oil-in-Water Emulsions

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Abstract

Partial coalescence or fusion of fat globules is a common form of destabilisation in food-related partially crystalline oil-in-water emulsions that generally causes thickening of the emulsion, reduced functionality and phase separation. Partial coalescence is particularly exacerbated by shear, temperature fluctuations and air incorporation. Each of which the food product may be exposed to during manufacture, storage, transport or end use leading most often to deleterious effects. One notable example of partial coalescence being desirable is during the manufacture of ice cream.

In order to better understand the factors affecting partial coalescence and their interactions, a systematic series of studies was undertaken on the shear stability of a model food-related partially crystalline oil-in-water emulsion. Shear-induced aggregation of 35 wt% partially crystalline oil-in-water emulsions was studied under conditions causing jamming of partially coalesced fat globule aggregates formed under steady shear. Emulsions with different interfacial compositions and solid fat content (~25–90%) were studied to probe their effect on the generation of a jamming transition over a range of shear rates (500–2000 s⁻¹). By displacing adsorbed sodium caseinate from the oil-water interface using Tween 20, partial coalescence sensitive emulsions were prepared with either mixed sodium caseinate-Tween 20 or Tween 20 dominated interfacial film compositions using 0.5 or 1.5 wt% Tween 20 respectively. Quiescently, the emulsions were stable with 0.5 wt% Tween 20 regardless of solid fat content. At 1.5 wt% or above, stability decreased with increasing solid fat content and Tween concentration. Under shear, partial displacement of adsorbed sodium caseinate by Tween 20 generally resulted in the formation of relatively stable aggregates whereas high displacement of protein led to the formation of less stable aggregates under shear.
The aggregation time of emulsions with Tween 20 dominated interfaces decreased with increasing solid fat content whereas for mixed sodium caseinate-Tween 20 emulsions it increased with increasing solid fat content. The extent of fat globule aggregation at low solid fat content was relatively low irrespective of Tween concentration, whereas at high solid fat content, the extent of aggregation varied considerably when interfacial composition was altered. Cryo-TEM micrographs of the fat globules revealed a relatively smooth surface regardless of composition indicating that fat crystal protrusion was not a major factor affecting the stability. These findings showed that interfacial protein functions both to regulate the formation of partially crystalline aggregates as well as the aggregate stability under shear. Furthermore, high solid fat content emulsions although low in liquid oil content were shown to be highly susceptible to partial coalescence when the adsorbed protein load was low.

The effect of polyoxyethylene sorbitan fatty acid esters (Tween) alone or in combination with sorbitan fatty acid esters (SPAN) on the shear stability of partially crystalline oil-in-water emulsions (35 wt% fat) was studied. Low molecular weight emulsifiers like Tweens and SPANS are often used to regulate the susceptibility of partially crystalline oil-in-water emulsions to aggregation and partial coalescence. It was found that emulsion stability increased with increasing chain length of the saturated Tween emulsifiers, while unsaturated Tween 80 was comparatively much more unstable than the saturated types of Tween. The effect of 1 wt% SPAN (SPAN 20, 40, 60 and 80) in the dispersed phase of emulsions containing different concentrations of Tween 80 (0.2–0.6 wt%) was also investigated. The emulsions showed sharp stability transitions from stable to unstable over the range of Tween 80 concentrations tested. All SPAN containing emulsions with 0.2 wt% Tween 80 were stable under shear however all emulsions with 0.6 wt% Tween 80 immediately aggregated when shear was applied. At
0.4 wt% Tween 80, the saturated long fatty acid chain length emulsifiers (SPAN 40 and 60) were in general much more stable compared to SPAN 20 and 80 containing emulsions. This study indicated that oil soluble SPAN emulsifiers with low and high melting points were similarly poor at preventing partial coalescence. Therefore, phase transitions were likely not a major contributing factor to emulsion stability.

Finally, the effects of Tween 20, 40, 60 and 80 on the stability of partially crystalline oil-in-water emulsions prepared with and without 1 wt% sodium caseinate were studied. Generally, 1 wt% sodium caseinate emulsions with the unsaturated emulsifier Tween 80 were the most unstable followed by the saturated emulsifiers Tween 20, 40 and 60 in order of increasing fatty acid chain length. Long chain saturated Tween emulsifiers (Tween 40 and 60) improved emulsion stability regardless of whether sodium caseinate was present indicating that alone these emulsifiers form more robust interfacial films compared to the shorter chain length Tween 20 and the unsaturated Tween 80. The Tween type dependent effect on supercooling and fat crystallization caused by interfacial heterogeneous nucleation was also studied using pulsed nuclear magnetic resonance. With sodium caseinate, the degree of supercooling decreased and the crystallization rate diminished with increasing saturated fatty acid chain length but only negligible changes were found without sodium caseinate. These findings indicate that long chain saturated Tweens improve emulsion stability by forming robust interfaces but with sodium caseinate also improve stability through interfacial heterogeneous nucleation. These novel findings provide guidance on how combinations of proteins and emulsifiers can be used to modify and control the stability of partially crystalline oil-in-water emulsions through their combined effects on fat crystallization and interfacial film properties.
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Fig. 6.3. Relationship between free fat content and peak viscosity of 35 wt% partially crystalline oil-in-water emulsions stabilized by 1 wt% sodium caseinate and 1.2 wt% (open symbols) or 1.6 wt% (closed symbols) Tween emulsifier. Solid lines are a guide for the eye. Symbols: (○) Tween 20; (□) Tween 40; (Δ) Tween 60.

Fig. 6.4. Effect of Tween type and sodium caseinate addition on the crystallization behaviour of partially crystalline oil-in-water emulsions (35 wt% fat) containing (A) 1% sodium caseinate and 0.8% Tween or (B) 0.8% Tween. Symbols: (○) Tween 20; (□) Tween 40; (Δ) Tween 60; (○) Tween 80; (+) 1% sodium caseinate only; (x) Emulsion temperature.

Fig. 6.5. Effect of Tween type and sodium caseinate addition on the onset crystallization temperature of partially crystalline oil-in-water emulsions containing 35 wt% fat. Colour scheme: (grey) 1% sodium caseinate and 0.8% Tween; (black) 0.8% Tween; (striped) 1% sodium caseinate.

Fig. 6.6. Comparison between the crystallization profiles of bulk fat and partially crystalline oil-in-water emulsions (35 wt% fat) containing 1% sodium caseinate and 0.8 wt% saturated or unsaturated Tween emulsifier. The measured bulk fat solid fat content values were multiplied by 0.35 (fat content of the emulsions) for ease of comparison with the emulsions. Symbols: (x) Bulk fat (70% hydrogenated palm kernel oil/30% canola oil); (Δ) Tween 60 - saturated; (○) Tween 80 - unsaturated.

Fig. 6.7. Correlation between the onset crystallization temperature and SFC of emulsions after 2000 s of holding time at 5 °C. The solid line is a linear regression line of best fit \( r^2 = 0.80 \). Filled symbols indicate emulsions contained 1 wt% sodium caseinate.
caseinate and 0.8 wt% Tween whereas empty symbols indicate emulsions contained only Tween. Symbols: (◊) Tween 20; (□) Tween 40; (Δ) Tween 60; (○) Tween 80; (X) 1% sodium caseinate only.

Fig. 6.8. Shear rate sweep at 5 °C of 35 wt% partially crystalline oil-in-water emulsions containing 1 wt% sodium caseinate and Tween 20 (A), Tween 40 (B) or Tween 60 (C) added after fat crystallization. Solid lines are a guide for the eye. Arrows indicate the direction of the shear rate sweep. Symbols indicate Tween concentration: (x) 0 wt%; (◊) 0.8 wt%; (○) 1.2 wt%; (□) 1.6 wt%.

Fig. 6.9. Shear rate sweep of 35 wt% partially crystalline oil-in-water emulsions containing 1 wt% sodium caseinate and different types of Tween emulsifier (1.6 wt%). Both the Tween emulsifiers and sodium caseinate stabilized emulsions were chilled at 5 °C for 24 h prior to mixing. Symbols: (◊) Tween 20; (□) Tween 40; (Δ) Tween 60; (○) Tween 80. Symbols: (A) Day 1; (B) Day 4; (C) Day 7.

Fig. 6.10. Shear rate sweep of 35 wt% partially crystalline oil-in-water emulsions containing 1 wt% sodium caseinate and different types of Tween emulsifier (1.6 wt%) at 5 °C. Emulsions were stored for 7 days at 5 °C prior to testing. Closed symbols indicate the Tween emulsifier was added prior to fat crystallization. Open symbols indicate Tween was added to a sodium caseinate stabilized emulsion chilled at 5 °C for 24 h prior. Symbols: (◊) Tween 20; (□) Tween 40; (Δ) Tween 60; (○) Tween 80; (x) 1 wt% sodium caseinate only (no Tween).

Fig. 6.11. Change in shear stability over time of 35 wt% partially crystalline oil-in-water emulsions under steady shear (2000 s⁻¹) at 5 °C stabilized by either 1.6 wt% Tween 20 (open symbols) or Tween 80 (closed symbols) and 1 wt% sodium caseinate.
The Tween emulsifiers were added to sodium caseinate stabilized emulsions chilled prior at 5 °C for 24 h. Symbols: (○) Day 1; (Δ) Day 4; (○) Day 7.

Fig. 7.1. Schematic diagram showing potential structural changes of two interfacial films in response to high and low solid fat content.
List of Abbreviations

HPKO – Hydrogenated palm kernel oil

T20 – Tween 20

T40 – Tween 40

T60 – Tween 60

T80 – Tween 80

SDS – Sodium dodecyl sulfate

PGFE – Polyglycerol fatty acid esters

SPAN – Sorbitan monoesters

Lactem – Lactic acid esters of mono and diglycerides

GMS – Saturated monoglyceride

GMU – Unsaturated monoglyceride

SSL – Sodium stearoyl lactylate

$d_{4,3}$ – Volume weighted mean diameter

$d_{3,2}$ – Surface weighted mean diameter

SFC – Solid fat content

HLB – Hydrophilic-lipophilic balance

TEM – Transmission electron microscopy

Cryo-TEM – Cryogenic transmission electron microscopy
AFM – Atomic force microscopy

NMR – Nuclear magnetic resonance