Fat Crystallisation: mechanism and methods for studying

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Fat Crystallisation:
mechanism and methods for studying

- **Polymorphism**
  - Basics

- **Crystallisation**
  - Nucleation, Growth and Supercooling
  - Post growth events, crystal ripening

- **Methods for studying**
  - Differential Scanning Calorimetry
  - Differential Thermal Analysis
  - Cooling Curves – Jensen & Shukoff
  - Solid Fat Content by NMR
  - Turbidity using light-scattering
Polymorphism

- Fats and triglycerides have different forms with different melting points
- Each form is called a polymorph and the phenomenon is called polymorphism: Greek ‘many forms’
- Fats & triglycerides occur in any one of three basic types: $\alpha$ (alpha), $\beta'$ (beta prime) and $\beta$ (beta)
- All fats have an $\alpha$ polymorph; some are $\beta'$ stable; some are $\beta$ stable
- Transitions go from $\alpha$ to $\beta'$ to $\beta$, in that order, which is the order of increasing stability.
**Vertical oscillating chains**

**Adjacent zigzags in different planes**

**Adjacent zigzags in different planes**

**Melting Points**

<table>
<thead>
<tr>
<th>α Vertical oscillating chains</th>
<th>β' Tilted chains with adjacent zigzags in different planes</th>
<th>β Tilted chains with all zigzags in same plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>54C (129F)</td>
<td>64C (147F)</td>
<td>73C (163F)</td>
</tr>
</tbody>
</table>
Polymorphism of Palm Oil & Fractions

DPT Heating  DPT Cooling

Liquid

Solid \( \beta'_2(sub-\alpha) \)

Solid \( \beta'_{1-2} \)

Solid \( \alpha-2 + \beta-2 \)

22°C  37°C  -15°C  -5 to 7°C

-5 to -10°C

from Persmark & Stahl, 1976
### Stable/Typical Polymorphs of common fats

<table>
<thead>
<tr>
<th>Fat</th>
<th>Polymorph</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cocoa Butter</td>
<td>β-3</td>
<td>Simple TAG mixture, mainly SOS type</td>
</tr>
<tr>
<td>Fully Hydrogenated Oils</td>
<td>β-2</td>
<td>Simple TAG mixture, mainly SSS type. Except hydrogenated PO is β’-2.</td>
</tr>
<tr>
<td>Milk Fat</td>
<td>β’-2</td>
<td>Complex TAG mixture</td>
</tr>
<tr>
<td>Lauric Oils (Palm Kernel &amp; Coconut)</td>
<td>β’-2</td>
<td>Complex TAG mixture</td>
</tr>
<tr>
<td>Partially Hydrogenated Oils</td>
<td>β’-2</td>
<td>Complex TAG mixture</td>
</tr>
<tr>
<td>Interesterified Oils</td>
<td>β’-2</td>
<td>Complex TAG mixture</td>
</tr>
<tr>
<td>Palm Oil</td>
<td>β’-2</td>
<td>Moderately simple TAG mixture, diacylglycerols important</td>
</tr>
<tr>
<td>Lard</td>
<td>β’-3</td>
<td>Moderately simple TAG mixture, mainly SSO type</td>
</tr>
</tbody>
</table>
Polymorphism: Margarine & shortenings

Normal (β')

Sandy (β)

1 scale unit = 100μ (Danisco TP 1504-2e)
Crystallisation

• Nucleation, Growth and Supercooling
• Post growth events, crystal ripening
Crystallisation: Supercooling & Supersaturation

Crystallisation occurs spontaneously

Crystallisation possible, but not certain

Super-saturated solutions above Solubility Curve

Solubility Curve/ saturated solution line
A crystal nucleus is the smallest crystal that can exist in a triglyceride mixture of a certain concentration and temperature.

Aggregates of molecules smaller than a nucleus are called embryos and will redissolve if formed.

A stable crystal will form only when the energy gain due to the heat of crystallisation exceeds that required to overcome the surface energy required to increase the surface.
Crystallisation: Nucleation - 2

• Homogeneous Nucleation takes place spontaneously in the bulk of the liquid, but does not occur in fats in practice.

• Instead, Heterogeneous Nucleation takes place and is initiated by solid particles such as dust, container wall or seed crystals.

• This is why emulsions are difficult to crystallise - each droplet is isolated from the others so that seeds cannot propagate.

• Secondary Nucleation occurs when small pieces break from existing crystals and act as nuclei for further crystallisation.
Crystallisation: Nucleation - 3

- The least stable, $\alpha$, polymorph has the lowest surface energy, as well as the lowest heat of crystallisation.
- Small differences in surface energy produce large differences in nucleation rate.
- Thus nucleation rates are in the order: $\alpha > \beta' > \beta$. 
Nucleation rate is greater for the less stable polymorph and is exponentially dependent on temperature.
Crystallisation: Growth

- Once a nucleus has formed, it starts to grow
- The growth rate is proportional to the degree of supercooling, i.e. lower temperature, and inversely proportional to the viscosity
- Like the nucleation rate, the growth rate depends on the polymorph crystallised
- The more stable the polymorph the less soluble it is and therefore the higher the growth rate, i.e.:
  \[ \beta > \beta' > \alpha \]
- But, rapid cooling of a fat always leads to the initial formation of unstable \( \alpha \) (or \( \beta' \)) crystals because nucleation is exponentially related to temperature
Crystallisation: Post-growth events - 1

- **Contraction**: Solid fat occupies about 90% of the volume of liquid fat.
- The amount of contraction depends on the SFC of the fat (the amount of fat crystallised) and the polymorph - more stable polymorphs are denser.
- **Agglomeration**: Crystals form agglomerates of spherulitic crystals with particle sizes of several hundred μm.
Crystallisation: Post-growth events - 2

- **(Ostwald) Ripening**: As nucleation, growth and agglomeration proceed, the overall supersaturation decreases and the critical size for a stable crystal or nucleus increases.
- Smaller crystals, which were stable at lower levels of supersaturation, now become unstable and redissolve.
- In theory, the process would continue indefinitely until eventually only one large crystal was left in the presence of a slightly supersaturated liquid.
- In practice, once crystals grow to about 10μm, the thermodynamic driving force is small.
Crystallisation: Summary

Liquid → Nucleation → Crystallisation → Separation → Agglomeration → Ripening

Adapted from: desmet ballestra
Methods for studying

Measure:

1. Heat evolved during crystallisation
   - Differential Scanning Calorimetry
   - Differential Thermal Analysis
   - Cooling Curves – Jensen & Shukoff

2. Increase in amount of fat crystals
   - Solid Fat Content by NMR
   - Turbidity using light-scattering
Crystallisation of milk fat – DSC cooling & heating curves

Sample
Reference
Sample Block (held at -90°C)
Computer
Resistance Thermometer

Cooling/crystallisation
Heating/melting

Temperature
Chart Recorder or Printer

Difference in heat required

0.5 mcal/sec
0.2 mcal/sec

Temperature (°C)
Crystallisation of cocoa butter – Jensen Cooling Curve

BSI Method 684:1.13

\[ T_{\text{max}} = \text{Temperature}(C) \text{ at Maximum} \]
\[ t_{\text{max}} = \text{Time}(\text{mins}) \text{ to Maximum} \]

\[ T_{\text{min}} = \text{Temperature}(C) \text{ at Minimum} \]
\[ t_{\text{min}} = \text{Time}(\text{mins}) \text{ to Minimum} \]
Crystallisation of palm oil – Shukoff Cooling Curve

IUPAC Method 2.132

- Thermometer
- Vacuum
- Oil

Temperature vs. Time

- $T_c, t_c$
- $T_{\text{max}}, t_{\text{max}}$
- $T_{\text{min}}, t_{\text{min}}$

Interesterified Palm Oil

Palm Oil

$\Delta T$
Crystallisation of 3 Fats - SFC Determination
(30C for 1 h tempering before measurement at 20C)

This fat mixture crystallises more slowly than the other two fats.
Turbidity using light-scattering - 1

From Smith, Cain & Talbot, 2005
Turbidity using light-scattering - 2

Graph showing:
- Temperature [°C] on the y-axis.
- Time (minutes) on the x-axis.
- Transmittance as a percentage on the y-axis.

Key points:
- Transmittance
- Temperature
- Clear point, $T_{CP}$
- Growth temp., $T_G$
- Cloud point, $T_C$
Fat Crystallisation: Summary

• **Polymorphism**
  – $\alpha$, $\beta'$ and $\beta$ in order of increasing stability
  – double and triple spacing
  – $\beta'$ preferred for many food fats

• **Crystallisation**
  – Nucleation followed Growth
  – $\alpha$ forms first

• **Methods for studying**
  – Heat evolved during crystallisation:
    • DSC, DTA, Cooling Curves
  – Increase in amount of fat crystals:
    • SFC, Turbidity
Thank you!
Any Questions?