Fat structuring with partial glycerides: effect on solid fat profiles

Jeroen Vereecken¹
Imogen Foubert¹
Wouter Meeussen²
Ans Lesaffer²
Koen Dewettinck¹

¹Ghent University, Ghent, Belgium
²Vandemoortele N.V., Izegem, Belgium
Introduction and background
Importance of the solid fat content

- SFC-profile: guideline in judging the suitability of an oil/fat blend for a particular application
- Importance for chocolate: - hardness
  - fast melting and flavor release
  - mouth feel at higher temperatures
- Importance for margarine/spreads: - spreadability at 5°C
  - oil exudation
  - thickness and mouth feel
- Wassell and Young (2007): Use of SFC to select TFA-substitutes
- Several studies: link between SFC and macroscopic properties
  => Fat structure based on SFC
Alternatives to crystalline fat

- In the past: fat structuring based on providing solid fat by regular vegetable oils and fats, especially palm oil fractions
- New trend: structuring of edible oils by alternatives to crystalline fat (Pernetti et al., 2007)
- Examples: - fatty alcohols
  - waxes
  - lecithin
  - sorbitan tristearate (STS)
  - phytosterols

=> totally different structure from regular triglycerides in fats and oils
Monoglycerides as solid fat providers

- One fatty acid on glycerol backbone ➔ amphiphilic neutral lipid molecule
- Generally known as emulsifiers in food products
- Other applications:
  - bread improver
  - antimicrobial agent
  - stabilization of foams
  - use in cosmetics
Monoglycerides as solid fat providers

- Some similarities between monoglycerides and triglycerides:
  - typical crystallisation and melting range
  - formation of a crystal network under certain conditions
  - characterized by a certain polymorphic behaviour
  - physical properties governed by the fatty acid profile

- Monoglycerides could be used as solid fat providers

- Less difference with triglycerides than other alternatives to crystalline fat

- Important property: higher melting point compared to triglycerides
Monoglycerides as solid fat providers

- Monoglycerides: high melting point compared to triglycerides

![Diagram showing the melting points of various monoglycerides and triglycerides with different fatty acids.]

- Fatty acid monoglyceride diglyceride triglyceride
- Melting point (°C)
- Palmitic (1 en 1,3)
- Palmitic (2 en 1,2)
- Palmitic and oleic
- Oleic (1 en 1,3)
- Oleic (2 en 1,2)
Objective of the research
Objective of the research

• Study of the feasibility of monoglycerides as solid fat providers
• Investigation of the solid fat profile of different monoglyceride blends
  ➢ Influence of the amount of saturated fatty acids
  ➢ Influence of the ratio of saturated fatty acids: palmitic/stearic, palmitic/behenic, stearic/behenic acid
  ➢ Influence of the ratio oleic/linoleic acid
  ➢ Influence of the amount of diglycerides
• Selection of the right monoglyceride mixture to provide solid fat to triglyceride systems
• Investigation of the influence of the addition of water
Experimental setup
Investigated samples

- Use of commercial monoglycerides: produced by glycerolysis of vegetable oils and distillation to raise monoglyceride content (> 90%)
- SM90FHPoS: based on fully hydrogenated palm stearin (saturated)
- SM90FHRso: based on fully hydrogenated rapeseed oil (saturated)
- SM90FHHer: based on fully hydrogenated high eruca rapeseed oil (saturated)
- UM90RRso: based on refined rapeseed oil (unsaturated)
- UM90RSfo: based on refined sunflower oil (unsaturated)
Investigated samples

- UM50HOSf: non distilled sample to study the effect of the amount of diglycerides
  - Based on high-oleic sunflower oil
  - Contains around 30% DGL
  - FA-profile: 81.20% oleic acid, 8.50% linoleic acid

- UM90HOSf: based on refined high oleic sunflower oil (unsaturated)
  - To study the effect of the addition of water

- Palm oil, palm stearin and rapeseed oil used as triglyceride providers
Performed analyses and methods

- Chemical analysis of commercial monoglycerides using:
  - FAME GC: Fatty acid profile
  - Carbon Number GC: Glyceride content
- Differential scanning calorimetry: reduction of the melting point of saturated monoglycerides in liquid oil
- pNMR: evolution of the solid fat content as a function of temperature
  - Determination of the solid fat profile
- Pulsed field gradient NMR: determination of the complete relaxation curve
  - Study of the influence of the addition of water
Results and discussion
Dilution of saturated monoglycerides with rapeseed oil

- Very high melting point of saturated monoglycerides compared to other glycerides
- Dilution of monoglycerides with rapeseed oil
- Analysis of the dilutions by DSC to derive the melting point of the system
- Ideal phase behaviour governed by the Hildebrand equation:

\[
\ln(x) = \frac{\Delta H}{R} \left( \frac{1}{T_{m}} - \frac{1}{T} \right)
\]

with \( x \) = mole fraction of the solid component in liquid oil
\( \Delta H \) = melting enthalpy of the solid component
\( R \) = universal gas constant = 8.314 J/mol.K
\( T_{m} \) = melting point of the non diluted solid component
\( T \) = melting point of the diluted solid component
Dilution of commercial monoglycerides with rapeseed oil

SM90FHRso: distilled monoglycerides based on fully hydrogenated rapeseed oil

Ideal phase behaviour following the Hildebrandt equation
## Fatty acid composition of the investigated samples

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>SM90FHPpos</th>
<th>SM90FHRso</th>
<th>SM90FHHer</th>
<th>UM90RRso</th>
<th>UM90RSfo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic (C16:0)</td>
<td>58.64</td>
<td>6.93</td>
<td>0.97</td>
<td>6.01</td>
<td>7.60</td>
</tr>
<tr>
<td>Stearic (C18:0)</td>
<td>39.03</td>
<td><strong>90.21</strong></td>
<td>4.17</td>
<td>1.71</td>
<td>4.71</td>
</tr>
<tr>
<td>Behenic (C22:0)</td>
<td>0.05</td>
<td>0.49</td>
<td><strong>84.54</strong></td>
<td>0.14</td>
<td>0.49</td>
</tr>
<tr>
<td>Oleic (C18:1)</td>
<td>0.00</td>
<td>0.06</td>
<td>0.06</td>
<td><strong>63.27</strong></td>
<td>22.41</td>
</tr>
<tr>
<td>Linoleic (C18:2)</td>
<td>0.00</td>
<td>0.06</td>
<td>0.00</td>
<td>17.79</td>
<td><strong>64.01</strong></td>
</tr>
<tr>
<td>SFA</td>
<td>99.79</td>
<td>99.67</td>
<td>97.98</td>
<td>8.80</td>
<td>13.18</td>
</tr>
</tbody>
</table>

=> Study of different effects, e.g. ratio P/S, by creating specific mixtures
Influence of SFA-content on solid fat profile

- Variation of SFA by mixing UM90RRso, SM90FHRso and SM90FHPos (ratio palmitic/stearic = 1)

Different regions:

- below 15°C: small difference between different SFA-levels
- between 15°C and 25°C: huge reduction of SFC for low SFA levels (< 40%)
- above 25°C: gradual reduction of SFC for higher SFA levels

For further experiments: 30% SFA (level used by health organizations)
Influence of palmitic (P)/stearic (S) ratio on solid fat profile

- Variation of palmitic/stearic ratio by mixing UM90RRso, SM90FHRso and SM90FHPo (SFA-content = 30%)

Effect at higher temperatures:
- lower SFC for higher ratios
- explanation: higher melting point of stearic acid compared to palmitic acid

Solid fat content (%)

P/S = 0.3

P/S = 1.7
Influence of palmitic (P)/behenic (B) ratio on solid fat profile

- Variation of palmitic/behenic ratio by mixing UM90RRso, SM90FHRso, SM90FHPos and SM90FHHer (P/S = 1 and SFA-content = 30%)

Same effect as for ratio P/S
Influence of stearic (P)/behenic (B) ratio on solid fat profile

- Variation of stearic/behenic ratio by mixing UM90RRso, SM90FHRso, SM90FHPQs, and SM90FHHer (P/S = 1 and SFA-content = 30%)

<table>
<thead>
<tr>
<th>Solid fat content (%)</th>
<th>0.3 S/B</th>
<th>0.4 S/B</th>
<th>0.5 S/B</th>
<th>0.6 S/B</th>
<th>0.7 S/B</th>
<th>0.8 S/B</th>
<th>0.9 S/B</th>
<th>1 S/B</th>
<th>1.5 S/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>50 S/B</td>
<td>90 S/B</td>
<td>10 S/B</td>
<td>20 S/B</td>
<td>20 S/B</td>
<td>50 S/B</td>
<td>90 S/B</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Same effect as for ratio P/S and P/B
Influence of oleic (O)/linoleic (L) ratio on solid fat profile

• Variation of oleic/linoleic ratio by mixing UM90RRso, UM90RSfo, SM90FHRso and SM90FHPoz (P/S = 1 and SFA-content = 30%)

Effect at lower temperatures:
- lower SFC for lower ratios
- explanation: higher melting point of oleic acid compared to linoleic acid
- no difference at higher temperature because of same level and type of SFA
Influence of diglycerides (DGL) on solid fat profile

• Variation of diglyceride content by mixing UM50HOSf, UM90RRso, UM90RSfo, SM90FHRso and SM90FHPo (P/S = 1, O/L = 3 and SFA-content = 30%)

Effect at lower temperatures:

➢ lower SFC for higher DGL content

➢ explanation: lower melting point of DGL compared to MGL

![Graph showing the influence of diglycerides (DGL) on solid fat profile. The graph indicates that lower SFC is observed for higher DGL content at lower temperatures, possibly due to a lower melting point of DGL compared to MGL.](image-url)
Search for the desired SFC-profile

- Variation of SFC at high temperatures by varying P/S, P/B or S/B ratio
- Variation of SFC at low temperatures by varying O/L ratio
  => specific SFC-profile obtained by selection of the right ratio of P/S and O/L
- Investigation of 4 new mixtures of SM90FHRso, SM90FHPos, UM90RRso and UM90RSfo with SFA-content = 30%
- H-L: high SFC at low temperatures, low SFC at high temperatures
- L-H: low SFC at low temperatures, high SFC at high temperatures
- H-H: high SFC at low temperatures, high SFC at high temperatures
- L-H: low SFC at low temperatures, low SFC at high temperatures
- Comparison with two triglyceride samples:
  - TGL sample 1: 45% palm oil, 35% palm stearin, 20% rapeseed oil
  - TGL sample 2: 27% palm oil, 21% palm stearin, 52% rapeseed oil
Evolution of the SFC-profile of four extreme mixtures

Aim: obtain SFC-profile TGL sample 1 by adding MGL-mixture to TGL sample 2
Monoglycerides as solid fat providers

Good correlation between TGL sample 1 and 50% mixture of H-L and TGL sample 2
Influence of water on solid fat profile of monoglycerides

- Addition of 2% water to a system with 20% UM90HOSf (based on high oleic sunflower oil) and 80% triglycerides (30% SFA)
Influence of water on solid fat profile of monoglycerides

- Addition of 2% water to a system with 20% SM90FHRso and 80% triglycerides (30% SFA)
Influence of water: difference between saturated (SM90FHRso) and unsaturated (UM90HOSf) monoglycerides

- Further investigation by a study of the complete relaxation curve (on which an SFC-measurement is based)
- Study at 4 temperatures: 5°C, 20°C, 35°C en 50°C
Relaxation curve UM90HOSf-mixture at 5°C

After addition of 2% water:

- Less strong solid signal
- Higher remaining liquid signal

⇒ more protons in the liquid state
Relaxation curve UM90HOSf-mixture at 20°C

After addition of 2% water:
- Less strong solid signal
- Higher remaining liquid signal
⇒ more protons in the liquid state
Relaxation curve UM90HOSf-mixture at 35°C

No difference after addition of 2% water
Relaxation curve UM90HOSf-mixture at 50°C

- No difference after addition of water
- No solid signal anymore
Relaxation curve SM90FHRso-mixture at 5°C

No difference after addition of 2% water
Relaxation curve SM90FHRso-mixture at 20°C

No difference after addition of 2% water
Relaxation curve SM90FHRso-mixture at 35°C

After addition of 2% water:
- Relaxation length of solid signal increased
- Protons in condition between solid and liquid state?
- Same liquid signal
Relaxation curve SM90FHRso-mixture at 50°C

After addition of 2% water:
- Relaxation length of solid signal increased
- Protons in condition between solid and liquid state?
- Same liquid signal
- Difference smaller as for 35°C
Conclusions
Conclusions

- Monoglycerides could be used as solid fat providers

- Modification of SFC-profile at high temperatures by varying ratio of saturated fatty acids, e.g. ratio P/S

- Modification of SFC-profile at low temperatures by varying ratio oleic versus linoleic acid or DGL-content

- Different signal when water is present
  - Reduction at low temperatures for unsaturated monoglycerides
  - Increase at high temperatures for saturated monoglycerides
Acknowledgements

- Vandemoortele N.V. is acknowledged for their scientific and financial collaboration and for providing the samples for this research
- Especially Wouter Meeussen, Ans Lesaffer and André De Laporte are acknowledged for their contribution to this research

![Vandemoortele Logo]

- Palsgaard is acknowledged for providing the sample UM90RRso

![Palsgaard Logo]
Thank you for your attention!
Fat structuring with partial glycerides: effect on solid fat profiles

Jeroen Vereecken¹
Imogen Foubert¹
Wouter Meeussen²
Ans Lesaffer²
Koen Dewettinck¹

¹Ghent University, Ghent, Belgium
²Vandemoortele N.V., Izegem, Belgium