Structure and Mechanical Properties of Fat Crystal Networks

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What is this?

margarine

How is it different from this?

olive oil
Stearic acid

Oleic acid

(Saturated fat)

(Unsaturated fat)
So, what is a fat after all?

*To the chemist and chemical engineer:*

- a complex mixture of high melting point triacylglycerols in low melting point triacylglycerols with complex phase behavior – all can be explained from knowledge of molecular composition and phase behavior (SFC and phase diagrams are king…)
To the crystallographer:

• a metastable polycrystalline material prone to recrystallization and fractionation – all can be explained from knowledge of polymorphism (XRD is king and DSC is queen…)
To the colloidal scientist:

• a colloidal gel (or colloidal crystal) composed of a network of polycrystalline fat particles which trap liquid oil within—all can be explained from knowledge of the mesoscale structure, i.e., colloidal sizes, interactions, distribution (rheometer is king and microscope is queen...)

To the consumer:

- something that makes you fat, but tastes good (cookies and chocolate rule…)

Factors affecting the texture of fats and fat-structured foods

1. Solid fat content

2. Primary crystal habit (polymorphism)

3. Nano and Microstructure
   a. crystallite morphology and size
   b. spatial distribution of network mass

4. Interparticle interaction forces
What controls hardness?

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>G' (Pa)</th>
<th>SFC (%)</th>
<th>F_y (N)</th>
<th>K (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.19E+07²</td>
<td>90.5²</td>
<td>602²</td>
<td>231²</td>
</tr>
<tr>
<td>15</td>
<td>2.64E+07²</td>
<td>90.5²</td>
<td>593²</td>
<td>223²</td>
</tr>
<tr>
<td>20</td>
<td>1.63E+07²</td>
<td>80.5²</td>
<td>312²</td>
<td>90²</td>
</tr>
<tr>
<td>24</td>
<td>4.08E+07²</td>
<td>60.0²</td>
<td>344²</td>
<td>96²</td>
</tr>
</tbody>
</table>

Means with a common superscript within a column are not significantly different (P>0.05).
Triacylglycerol Molecules

Crystal Clusters

Crystal Network

Fat

Solid Fat Content

Polymorphism

Molecular Structure

Macroscopic World

> 0.2 mm

Microstructure

0.1-200 μm

Nanostructure

0.4–100 nm

Rheology

Mechanical Strength

Sensory Impressions

Heat, mass, momentum transfer

Heat, mass, momentum transfer

Heat, mass, momentum transfer

Heat, mass, momentum transfer

Heat, mass, momentum transfer
Triacylglycerols—Molecular Structure

Triacylglycerol = glycerol + 3 fatty acids
### Fatty Acids and Triacylglycerol Types

<table>
<thead>
<tr>
<th>Fatty Acids</th>
<th>Long-Chain Saturated</th>
<th>14:0, 16:0, 18:0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Medium-Chain Saturated</td>
<td>8:0, 10:0, 12:0</td>
</tr>
<tr>
<td></td>
<td>Short-Chain Saturated</td>
<td>4:0, 6:0</td>
</tr>
<tr>
<td>Mono-Unsaturated</td>
<td>18:1</td>
<td></td>
</tr>
<tr>
<td>Poly-Unsaturated</td>
<td>18:2, 18:3, 22:6</td>
<td>(cis vs. trans)</td>
</tr>
<tr>
<td>Geometric Isomers</td>
<td>(cis vs. trans)</td>
<td></td>
</tr>
<tr>
<td>Positional Isomers</td>
<td>(ω-3,6,9)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Triacylglycerols</th>
<th>Simple Homogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mixed</td>
</tr>
<tr>
<td></td>
<td>Complex and varied positional</td>
</tr>
<tr>
<td></td>
<td>distribution of fatty acids on</td>
</tr>
<tr>
<td></td>
<td>TAG molecule.</td>
</tr>
</tbody>
</table>
Triacylglycerol Crystallization Process

$T > T_m$  Isotropic Melt

Decrease temperature below melting point of solid into metastable region (where the material is undercooled or supersaturated)

$T < T_m$  Crystalline Solid

T<T_m
Isothermal

Quasi-isothermal

Non-isothermal
Driving force for nucleation and crystallization is the degree of undercooling:

\[ \Delta T = T_m - T_{\text{set}} \]

Defines which polymorph will be formed and determines rates of nucleation and crystallization.
Temperature/supersaturation effect

$\alpha$-polymorph, 5$^\circ$C, $\Delta T=29^\circ$C

$\beta'$-polymorph, 25$^\circ$C, $\Delta T=9^\circ$C
A difference in chemical potential: the driving force for crystallization

\[ \mu_i = \left( \frac{\partial G}{\partial n_i} \right) T, P, n_{j \neq i} \]

\[ \Delta \mu = \mu_l - \mu_s = \frac{\Delta H}{T_f} \Delta T \]

\[ \Delta \mu = -RT \ln \beta \]

\[ \beta_i = \frac{[c_i]}{[c_i^*]} \]

\[ \ln \beta = -\frac{\Delta \mu}{RT} \]
A “proper” crystallization table for FHCO crystallized at 30°C

<table>
<thead>
<tr>
<th>FHCO (%)</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_m$ (kJ.mol$^{-1}$)</td>
<td>32.5</td>
<td>61.4</td>
<td>73.4</td>
<td>95.4</td>
<td>106.8</td>
<td>120.3</td>
<td>129.6</td>
<td>148.4</td>
<td>164.9</td>
</tr>
<tr>
<td>$T_m$ (K)</td>
<td>333.3</td>
<td>336.5</td>
<td>337.4</td>
<td>338.8</td>
<td>340.7</td>
<td>342.0</td>
<td>344.2</td>
<td>344.4</td>
<td>344.9</td>
</tr>
<tr>
<td>$\Delta \mu$(kJ.mol$^{-1}$)</td>
<td>10.06</td>
<td>11.52</td>
<td>11.93</td>
<td>12.55</td>
<td>13.41</td>
<td>13.98</td>
<td>14.94</td>
<td>15.05</td>
<td>15.25</td>
</tr>
<tr>
<td>$\ln \beta$</td>
<td>3.9</td>
<td>4.4</td>
<td>4.6</td>
<td>4.8</td>
<td>5.1</td>
<td>5.4</td>
<td>5.7</td>
<td>5.8</td>
<td>5.9</td>
</tr>
</tbody>
</table>
Energetics of Nucleation

\[ \frac{\partial [\alpha_s]}{\partial t} = k[\alpha^*_L] = k[\alpha_L]e^{\frac{\Delta G^*}{RT}} \]
Gibbs-Thompson Equation

$$\Delta G_n = A_n \gamma - V_n (\Delta \mu / V_m)$$
Quantification of crystallization behavior

1. Growth mode (Avrami model)

\[
\frac{SFC(t)}{SFC(\infty)} = 1 - e^{-kt^n}
\]

- \( k \) - rate constant of crystallization
- \( n \) - dimensionality of growth and the type of nucleation

2. Nucleation (\( \tau, \Delta G_c \) - Fisher-Turnbull model)

\[
J = \frac{NkT}{h} e^{-\left(\frac{\Delta G_c + \Delta G_d}{kT}\right)}
\]

- \( \Delta G_c \) - activation free energy of nucleation
- \( \Delta G_d \) - activation free energy of diffusion
Phase Technology Cloud Point Analyzer
Fisher-Turnbull approach

\[ \ln(\tau T) \sim -\ln \frac{Nk_B}{h} + \frac{16\pi \delta^3 (V_m^s)^2 T_f^2}{3k_B \Delta H_f^2} \left( \frac{1}{T(\Delta T)^2} \right) \]

\[ m = \frac{16\pi \delta^3 (V_m^s)^2 T_f^2}{3k_B \Delta H_f^2} \]

\[ \Delta G_n^\# = \frac{mk_B}{(\Delta T)^2} \]
Interfacial Tension

$$
\delta = \left( \frac{3mk_B \Delta H_f^2}{16\pi (V_m^s)^2 T_f^2} \right)^{1/3}
$$

Molar volume (m$^3$ / mol) = \( \frac{MW \, (g / mol)}{density \, (g / ml)} \) \( (1 \cdot 10^{-6} \, m^3 / ml) \)
Induction Times as Determined from Crystallization Curves at Various Temperatures...cocoa butter
Quantification of crystallization behavior

1. Growth mode (Avrami model)

\[
\frac{SFC(t)}{SFC(\infty)} = 1 - e^{-kt^n}
\]

- \(k\) - rate constant of crystallization
- \(n\) - dimensionality of growth and the type of nucleation

2. Nucleation (\(\tau, \Delta G_c\) - Fisher-Turnbull model)

\[
J = \frac{NkT}{h} e^{-\left(\frac{\Delta G_c + \Delta G_d}{kT}\right)}\sim
\]

- \(\Delta G_c\) - activation free energy of nucleation
- \(\Delta G_d\) - activation free energy of diffusion
**Table 6**: Avrami exponent values for the different types of growth and nucleation (Sharples, 1966)

<table>
<thead>
<tr>
<th>Avrami Exponent</th>
<th>Various types of growth and nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3 + 1 = 4$</td>
<td>Spherulitic growth from sporadic nuclei</td>
</tr>
<tr>
<td>$3 + 0 = 3$</td>
<td>Spherulitic growth from instantaneous nuclei</td>
</tr>
<tr>
<td>$2 + 1 = 3$</td>
<td>Disc-like growth from sporadic nuclei</td>
</tr>
<tr>
<td>$2 + 0 = 2$</td>
<td>Disc-like growth from instantaneous nuclei</td>
</tr>
<tr>
<td>$1 + 1 = 2$</td>
<td>Rod-like growth from sporadic nuclei</td>
</tr>
<tr>
<td>$1 + 0 = 1$</td>
<td>Rod-like growth from sporadic nuclei</td>
</tr>
</tbody>
</table>
n=4

n=1
$k = 0.00103 \text{min}^{-1.5}$
$n = 1.50$
$SFC_\infty = 67.7\%$
Linearization of the Avrami Model

\[ \ln \left( - \ln \left( 1 - \frac{SFC}{SFC_{\text{max}}} \right) \right) = \ln(k_A) + n \ln(t) \]
Multiple crystallization steps

\[ SFC = SFC_o + \sum_{i=1}^{n} SFC_{\text{max},i} (1 - e^{-k_i t^{ni}}) \]
Graphs showing:

1. \( n_1 = 1.4, k_1 = 0.00013, Y_1 = 20.3 \)
2. \( n_2 = 2.6, k_2 = 0.20, Y_2 = 16.2 \)
3. \( n = 0.6, k = 0.11, Y_m = 49.4 \)
Avrami Exponent vs. Crystallization Temperature....cocoa butter
Chemical Potential and Viscosity

\[ J_{\text{nucleation}} \rightarrow f(\Delta \mu) \]
\[ J_{\text{growth}} \rightarrow f(\Delta \mu, \eta^{-1}) \]
\[ D \rightarrow f(\eta^{-1}) \]

Thoughts: 
- nucleation and growth rates are strongly influenced by chemical potential
- molecular, particle and cluster diffusion strongly influenced by viscosity (building mesoscale)
- shear will not affect liquid oil viscosity (Newtonian)
- shear will affect momentum transfer but only when diffusing objects are large enough*

*May have to include in future as another state variable
20% FHSO (SFC=99.2%) in HOSO @ 40°C
\[ \Delta \mu_i = RT \ln \beta_i \]

\[ \beta_i = \frac{[c_i]}{[c^*_i]} = \frac{SFC_{\max,sol}^{T_{\text{final}}} - SFC_{\text{sol}}^{T(t)}}{x \cdot SFC_{\text{neat}}^{T_{\text{final}}} - SFC_{\max,sol}^{T_{\text{final}}}} \]
Let's consider the actual solubility at each temperature on the way to equilibrium. The phase trajectory shows how the chemical potential \( \mu \) changes with respect to the viscosity \( \eta \), and the critical viscosity \( \eta_{cr} \) is indicated. The graph compares the chemical potential changes for a waterbath and an incubator.
Factors affecting the texture of fats and fat-structured foods

1. Primary crystal habit (polymorphism)

2. Solid fat content

3. Nano and Microstructure
   a. crystallite morphology and size
   b. spatial distribution of network mass

4. Interparticle interaction forces
SFC is one of the most influential factors in determining fat mechanical properties, but Not the only one!

Milkfat crystallized Statically at 5°C

**Hardness Index**

\[ HI = \frac{\text{mass of cone (g)}}{\text{depth of penetration (mm)}} \]
Phase Behavior

Fats are mixtures of lipids, predominantly triacylglycerols, but also contain minor polar components such as diacylglycerols, monacylglycerols, free fatty acids, phospholipids, sterols, etc.

Continuous solid solution (mixed crystals), eutectic, monotectic (partial solid solution), compound formation phase behaviors are commonly observed.
Continuous solid solution: SSS/ESS, POS/SOS

Eutectic behavior: PPP/SSS, EEE/SOS, POS/PSO, PPP/LLL, PPP/SOS

Compound formation: SSO/SOS, POP/OPO

Monotectic behavior: SSS/OOO, SSS/LLL, PPP/POP, SSS/SOS
Conditions for fat compatibility

1. Equivalent thermal properties
   Melting points
   Melting and solidification ranges
   SFC

2. Similar molecular size, shape and packing
   To allow isomorphous replacement or formation of a single lattice unit in mixtures

3. Similar polymorphism
   Transformation from stable to unstable forms should occur as readily for binary mixtures as with individual components
Continuous solid solution – compatible

Eutectic – incompatible (minima)

Monotectic – significant amounts of lower melting component solubilized by higher melting component. Eutectic point close to m.p. of lower melting component; partial solid solution

Compound formation (maxima)
Lever Rule – Phase composition

\[ X_{\text{solid}} = \frac{w_o - w_l}{w_l - w_s} \]

\[ X_{\text{liquid}} = \frac{w_s - w_o}{w_l - w_s} \]
“Eutectic,” in Greek, means “easily melted” and indicates a melting point lower for the solution than that of the individual pure products in solution.

Hildebrand equation: $\ln(x_i) = \Delta H_i / R \left(1/T_m - 1/T\right)$
POP-OPO Molecular Compounds
Ideal Solubility – TAGs are ideally soluble in liquid state

\[
\ln(x_i) = \frac{\Delta H_i}{R} \left( \frac{1}{T_m} - \frac{1}{T} \right)
\]

\[
T_m^{-1} = \left( \frac{\Delta H_m}{R} \right)^{-1} \ln(1 - \Phi)
\]

\[
\Delta H_{m,1} = 37.238 \text{ kJ/mol}
\]

\[
\Delta H_{m,2} = 5.322 \text{ kJ/mol}
\]

\[
\Phi_c \approx 0.15
\]
Bruker Minispec pNMR
Magnetization Signal Intensity

Pulse $t_B=10$

Solid – liquid components (total hydrogen content)

Liquid component only $t_A=70$

Time ($\mu$s)
How to construct Lipid phase diagrams

1- Prepare dilutions of the two fats
2- Measure SFC as a function of temperature for each dilution, create a spline and obtain temperatures corresponding to a series of SFCs (every 5%)

3- Plot Temperature vs. Composition
Iso-Solid graphic

Top line is 0% SFC:liquidus
Bottom line is 95 % SFC:solidus

partial solid solution behavior
MMF + HMF: Monotectic, compatibility

HMF + CB: partial compatibility

MMF + CB: EUTECTIC, incompatibility
Dropping point machine
Holder to slide inside

“Cup” for the sample

Holder to “catch” the first drop of melted sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature for the first drop</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 % A</td>
<td>34 °C</td>
</tr>
<tr>
<td>60 % A</td>
<td>32 °C</td>
</tr>
</tbody>
</table>
Dropping point machine use for solubility

![Graph showing the dropping point (°C) for different milkfat fractions.](image-url)
SFC influences hardness...
Microstructure
Brightfield microscopy

Bright field microscopy is the simplest of all the light microscopy techniques. Sample illumination is via transmitted white light (typically from a halogen microscope bulb), illuminated from below and observed from above.
Polarized light Microscope
Why can we see fat crystals?

The polarized light microscope is designed to observe and photograph specimens that are visible primarily due to their optically anisotropic character. In order to accomplish this task, the microscope must be equipped with both a polarizer, positioned in the light path somewhere before the specimen, and an analyzer (a second polarizer), placed in the optical pathway between the objective rear aperture and the observation tubes or camera port. Image contrast arises from the interaction of plane-polarized light with a birefringent (or doubly-refracting) specimen to produce two individual wave components that are each polarized in mutually perpendicular planes. The velocities of these components are different and vary with the propagation direction through the specimen. After exiting the specimen, the light components become out of phase, but are recombined with constructive and destructive interference when they pass through the analyzer. Polarized light is a contrast-enhancing technique that improves the quality of the image obtained with birefringent materials when compared to other techniques such as darkfield and brightfield illumination, differential interference contrast, phase contrast, Hoffman modulation contrast, and fluorescence.

http://www.microscopyu.com/tutorials/java/polarized/crystal/index.html
<table>
<thead>
<tr>
<th>Characteristic</th>
<th>α form</th>
<th>β’ form</th>
<th>β form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>5 µm</td>
<td>1-5 µm</td>
<td>&lt;50 µm</td>
</tr>
<tr>
<td>Shape</td>
<td>platelets</td>
<td>Tiny needles</td>
<td>Long needles</td>
</tr>
</tbody>
</table>
Time – Temperature State Diagram for the Polymorphism of Statically Crystallized Cocoa Butter
The $\alpha$ form
The $\beta'$ form
The $\beta$ form
Growth of a Polycrystalline Fat Crystal Network
Growth of a fat crystal network
Effect of cooling rate

- 0.4°C/min
- 1.2°C/min
- 6.0°C/min
Effect of Surfactant Addition

0.1% vs. 0.5% Tween 60
Temperature Effect

5°C

25°C
Effect of film size on slide

170um

20um
Atomic Force microscope
Cocoa Butter Fat Crystal Network Visualized using AFM
Rheology of Fats
Small Deformation Dynamic Controlled Stress Rheometer

TA AR2000
Viscoelasticity of Fats

$G''/G' \sim 0.1$

Shear strains of $\sim 0.1\%$ or less

$G'$ frequency-independent
The graph shows the relationship between Stress (Pa) and Storage Modulus (Pa) with Strain (%) as a function. The graph includes data points represented by circles and triangles, with error bars indicating variability. The y-axis represents Storage Modulus (Pa) ranging from 0 to 300,000,000, and the x-axis represents Stress (Pa) ranging from 0 to 10,000.
Large Deformation Mechanical Tests
Displacement (mm)

Force (N)

Yield Force (N)

Yield Work (N mm)

Yield deformation (mm)
Cone penetrometer
Drop the cone for 5 s into the sample.

Measure the penetration depth.
Repetitions
At least 3
Ideal measurement: one “poke” in a container with walls 2.5 cm away from the indentation.

Depth of penetration (1/10 mm)

Hardness Index
HI = mass of cone (g) / depth of penetration (1/10mm)

Yield Value
\[ Y = \frac{K \times W}{x^{1.6}} \]

Y = Yield value g/cm²
K = constant depending on the geometry of the cone used
W = weight of cone and all parts belonging to the shaft
p = penetration depth in 0.1 mm

J.Haighton
Cone penetrometer – results for a mix
Modeling the microstructure of a fat
MECHANICAL PROPERTIES OF PLASTIC-DISPERSE SYSTEMS AT VERY SMALL DEFORMATIONS

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Received August 2, 1960; revised November 15, 1960

ABSTRACT

A system containing flocculated solid particles in a liquid shows viscoelastic behavior at very small deformations. A model is described by means of which the elastic modulus of the system can be correlated with the forces acting between the particles. It is assumed that these forces are due to van der Waals-London attraction, and their contribution to the modulus is calculated. A method is indicated which allows the contribution of the van der Waals-London forces to the modulus of the material to be measured under specified conditions. Experiments on materials containing fat crystals in oil show agreement between predicted and experimental values for this contribution, if it is assumed that the solid particles in the aggregate approach each other to a distance of about 10 Å.

The energy content of the van der Waals-London bonds in these materials has been estimated from measurements of their rate of breaking in creep experiments, i.e., under the influence of a constant, low shearing stress. The energy content of about 30 kT-units is in satisfactory agreement with the results of stiffness measurements.

List of Symbols

\[ G = \frac{5AD^{0.5}}{24\pi H_o^{3.5}} \Phi \]

\( A \) = Hamaker's constant determining van der Waals-London attraction (erg).

\( B_2 \) = Abbreviation defined in Eq. [16].

\( D \) = Average particle diameter (cm.).

\( \Delta h^i \) = Free energy of activation for breaking a bond of type \( i \).

\( f_i \) = Average force exerted on bond of type \( i \).

\( G' \) = Shear modulus (dynes/cm.\(^2\)).
$G' \sim \Phi$

A milkfat

B palm oil

C tallow

D lard
Network model needs to take into account the presence of particle (crystal) aggregates.
G~Φ for single particle network does not provide satisfactory description of system’s behavior

Rather: G~Φ

Several parameters that determine the state of aggregation are lumped together into one dimensionless ‘scaling factor’

He also suggests that μ~N

Good agreement with experiments
The low values of the correction factor in dispersions containing a smaller number of larger particles suggest the presence of aggregates containing up to $10^6$ particles. This is what one would expect on the basis of kinetic arguments: The initial rate of aggregation is proportional to the square of the particle concentration. In a sufficiently concentrated suspension (i.e., large $N$) the aggregation is essentially finished before the particles have had time to migrate toward centers of aggregation. The result is a uniform distribution of single particles in the network. If aggregation proceeds more slowly there is ample time for the formation of the inhomogeneous structure that is commonly found in flocculated dispersions.

The state of aggregation in a flocculated dispersion must depend on the conditions prevailing during and immediately prior to its production. In particular, the amount and type of agitation and the magnitude of the attractive force will affect the aggregation parameters and hence the mechanical properties of the material obtained. The results presented in Fig. 1 had been obtained with a minimum of agitation during flocculation. Dispersions of carbon particles in oil or in water, and emulsions, require more agitation. It is, therefore, not surprising that such dispersions exhibited much less aggregation than would be expected on the basis of the correlation shown in Fig. 1.

REFERENCES

The fractal nature of fat crystal networks

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Abstract

Glycerol tristearate aggregates in olive oil are shown to have a fractal structure. The fractal dimension, as deduced from light scattering experiments, is \( d = 1.7 \), which is in line with predictions of recently developed aggregation models. The fractal dimension increases with time to \( d = 2.0 \), indicating that the aggregate structure becomes more compact as a result of ageing. No influence of the application of shear on the structure of the aggregates is detected. An interpretation of rheological data for glycerol tristearate networks is presented in the framework of fractal theory. It is shown that the elastic modulus and the yield stress vary with particle concentration according to a power law. From the power-law dependence the fractal dimension of the aggregates is calculated to be \( d = 2.0 \), in line with the results of light scattering experiments.

Keywords: Fat crystals; fractal aggregates; light scattering; rheology.

Introduction

In many food products, the formation of a network of crystallized fat particles is essential. The network provides firmness or solid-like behaviour to products such as margarines or spreads. The mechanical properties of fat networks have been explained in terms of a simple network model, developed originally by van den Tempel [1] and elaborated by others [2–4]. In this model, the network is composed of straight chains of aggregated fat particles, held together by attractive van der Waals forces. The model correctly predicts the number of magnitude of the elastic modulus for a number of systems and has been the basis for a description of time effects in dynamic measurements. However, the simple network model also shows some deficiencies. For example, the elastic modulus and the yield value of the network are predicted to vary linearly with the volume fraction of dispersed particles, whereas experiments have shown a much stronger dependence [2,3,5]. It was realized that this discrepancy is related to the assumption that the fat particles are arranged into straight chains. In reality, the network is built from aggregates of fat particles. Several attempts have been made to improve the network model by taking into account the presence of aggregates [6–8]. A quantitative description of the network properties, however, was hampered by the complex and random nature of the structure of the aggregates.

Considerable progress has been made recently after introduction of the fractal concept [9]. This concept permits a quantitative description of the structure of aggregates through the fractal dimension, \( d \), which quantifies the way in which the mass, \( M \), of a cluster increases with its size \( R \), \( M \sim R^d \). For aggregates grown by the diffusion-limited mechanism \( d = 1.75 \); aggregates grown by the reaction-limited mechanism have a slightly higher fractal dimension, \( d = 2.0 \) [9]. Light scattering has

\[
G' \sim \Phi^\mu
\]

\[
\mu = \frac{d + x}{d - D}
\]

\[
\mu \approx \frac{4.3}{3 - D}
\]
Heertje, I. (1993)

Microstructural Studies in Fat Research

Food Structure 12, 77-94
Microstructural studies in fat research

Tional LM, a disturbance-free observation of specimens, which is very important in the study of shear-sensitive samples such as fat spreads in general and low-fat spreads in particular. The confocal technique has also been used in the study of the competitive adsorption of emulsifiers.

Specific EM preparation techniques and their characteristics have been amply discussed (Brooker, 1990; Buchheim, 1982; deMan 1982; Heertje et al., 1987a; Kalab, 1983; Sargent, 1988). In the investigations described in the present paper, most of those EM techniques have been applied. They comprise:

- Transmission electron microscopy (TEM) of thin sections;
- Transmission electron microscopy of freeze-fractured and freeze-etched material (FFEM);
- Cryo-Scanning electron microscopy (Cryo-SEM) of freeze-fractured, freeze-etched, and de-oiled material.

The latter option has been developed in order to arrive at a proper observation of the product structure, in particular, the fat crystalline network, of fat spreads (Heertje et al., 1987a). Otherwise, the liquid oil in fat spread compositions would completely obscure proper observation of the solid fat crystalline matrix.

Shortenings

Shortenings have the simplest product structure of all fat spreads, because they are only composed of liquid oil and solid fat crystals. Depending on the application, the solid/liquid ratio can be varied. Appropriate preparation techniques, extracting the oil from the product, revealed that the fat crystals form a three-dimensional crystalline network (Heertje et al., 1987a). An example of such a network structure is shown in Fig. 2, which indicates the presence of sintered crystals while sheet-like aggregates and crystal bridges are formed. Depending on processing, also other types of aggregation can be discerned. When a fat blend is completely crystallized in the processing equipment (Heertje et al., 1988), a homogeneous structure of small connected plate-like aggregates is formed (Fig. 3a), whereas partial crystallization in rest leads to a non-homogeneous structure of large clusters interconnected by crystal bridges (Fig. 3b). Both products have also been rheologically characterized by parallel plate compression. From the resulting stress-strain curves, the highest value of \( g_{\text{max}} \) (greatest hardness) and shows the ease of compression.

Figure 5. Influence of deformation (parallel plate compression) on microstructure. a. Before deformation, crystalline clusters interconnected by a fat crystalline network (arrows). b. After deformation, more open structure between the clusters.

The product with the homogeneous microstructure has the highest value of \( g_{\text{max}} \) (greatest hardness) and shows the ease of compression.
Support for the view of fats as crystallite fractal gels grows

Johannsson also shows that:

\[ \xi \sim \Phi^{1/(D-d)} \]
Weak-link vs. Strong Link

High SFC vs. Low SFC

Fractal analysis explains the softening observed in milkfat upon chemical interesterification

Is Plastic Fat Rheology Governed by the Fractal Nature of the Fat Crystal Network?

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ABSTRACT: The rheological properties of interesterified and noninteresterified butterfat–canola oil blends do not seem to be strongly related to either solid fat content (SFC) or crystal polymorphic behavior, but rather to the microstructure of the fat crystal network. The microstructure of the fats was quantified by using fractal geometric relationships between the elastic modulus ($G'$) of the fats and their SFC values using the approach of Shih, W.H., W.Y. Shih, S.I. Kim, J. Liu, and I.A. Akssay [Phys. Rev. A 42:4772–4779 (1990)] for weak-link regimes. Chemical interesterification decreased the fractal dimension of the fat crystal network from 2.46 to 2.15. We propose that fat microstructure, as quantified by a fractal dimensionality, could be modified to attain specific rheological properties.


KEY WORDS: Butterfat, fractal dimension, interesterification, plastic fats, rheology, spreadability, texture.

The formation of a fat crystal network is of key importance in the manufacture of plastic fats because it provides firmness or solid-like properties (viscoelasticity) (1). This network can be visualized as being built from aggregates of fat particles (1) rather than straight chains of fat particles (2), and can be thought of as a colloidal aggregate, analogous to a protein gel. Each of the fat particles is, in turn, comprised of several aggregated fat crystals. The quantitative description of such a complex, aggregated “random” system is difficult. Recently, fractal geometry has proven extremely helpful in the characterization of these fractal objects (see Theoretical considerations section).

Work by our group has recently concentrated on improving the rheological properties of butterfat by blending with canola oil and chemical interesterification of these blends (3–5). Our aim was to improve the cold-temperature spreadability of butter. To understand which parameters control the rheology of this plastic fat, a comprehensive study on the melting properties, microstructure, and mechanical characteristics of these blends was undertaken (3–5).

During these studies, we noticed some interesting trends. First, chemical interesterification of butterfat or butterfat–canola oil blends did not substantially decrease the solid fat content (SFC) of butterfat or the blends—the maximum decrease being ~5% (3). Second, melting characteristics, as determined by differential scanning calorimetry, were similar for interesterified and noninteresterified blends in the range of 60–100% (w/w) butterfat (3).

However, when studying the rheological properties of the blends, we noticed that the hardness index, as determined by cone penetrometry, of the blends containing 90 and 80% (w/w) butterfat dropped by 63 and 59%, respectively, after interesterification, relative to their noninteresterified counterparts (5). Hardness of the 100 and 70% butterfat blends dropped 21 and 30%, respectively (5). These drastic changes could not be correlated with their SFC values. Further rheological studies showed that the storage modulus ($G''$), or elasticity, of the interesterified blends was lower relative to their noninteresterified counterparts (5).

Light and scanning electron microscopy of the blends showed that the fat crystal morphology (size and shape) and crystal arrangement had changed drastically after interesterification (4). In general, both incorporation of canola oil and interesterification led to the creation of larger spherulitic particles. X-ray diffraction studies of the blends confirmed that the predominant crystal form of butterfat and butterfat–canola oil blends was the $B$ form. Even though small changes were observed in butterfat crystal polymorphism due to canola oil incorporation and/or interesterification, no drastic changes in the polymorphic behavior of the fat crystals were observed (4).

All of these results pointed toward the possibility that it is not the actual SFC and/or crystal polymorphic form that determines the mechanical properties of butterfat–canola oil blends, but rather the macroscopic structure of the network of fat crystals in liquid oil (see figures in Ref. 4). The problem remained how to describe the structure of a fat crystal network quantitatively.

In this paper, we report on the use of fractal geometry to characterize the structure of the fat crystal network in butterfat–canola oil blends to determine the effects of interesterification on the fractal nature (structure) of the plastic fat. We propose that the mechanical properties (elasticity) of plastic fats are linked to the geometry of the fat crystal network.

Theoretical considerations. The purpose of this section is to briefly introduce the reader to the topic of fractal geometry and its application in the study of plastic fat structure. It is our experience that studies available in the literature fail to jus-
Fractal nature of fat crystal networks
Physical Review E 59: 1908

The quantification of microstructure in fat crystal networks is studied using the relationship of the shear elastic modulus ($G'$) to the volume fraction of solid fat ($\Phi$) via the mass fractal dimension ($D_m$) of the network. Results from application of a scaling theory (weak-link regime theory), developed for colloidal gels, to the microstructure of fat crystal networks are presented and discussed. A method to measure true fractal dimensions and chemical length exponents or backbone fractal dimensions ($z$) from in situ polarized light microscopy (PLM) images of the microstructural networks of fat crystals is developed and applied to the fat systems studied. Fractal dimensions measured from in situ PLM images of the various fat systems are in good agreement with fractal dimensions measured using rheological measurements and the weak-link regime theory (percent deviations range from 0.40% to 2.50%). The crystallization behavior of the various fat systems is studied using differential scanning calorimetry, and the potential for altering $G'$ by changing crystallization conditions using the fractal dimension of the network as an indicator is discussed. [S1063-651X(99)00502-4]

PACS numbers: 61.40.-j, 61.14.-e

1. INTRODUCTION

Some of the most important quality characteristics of fat-containing food products depend on the macroscopic properties of the fat crystal network formed within the finished product. Some of these characteristics include the spreadability of margarine, butter, and spreads, as well as the snap of chocolate. Predicting the macroscopic properties of fat crystal networks within these products is therefore important.

It has been previously established that the hardness of a fat, as determined by large-scale rheological analyses such as cone penetrometry, is directly correlated to the hardness determined by sensory analysis [1–4] (in cone penetrometry measurements, strain levels are of the order of 16%, hence the large-scale classification). Furthermore, measurements in our laboratory indicate that there exists a direct relationship between the elastic modulus (storage shear modulus) of a fat and its hardness index, as determined by cone penetrometry measurements (measurement of shear storage modulus is a small-scale rheological measurement with strain levels of the order of 0.5%). Therefore, the elastic modulus of a fat crystal network is an indicator of the macroscopic consistency of that network.

This paper describes an attempt to utilize scaling theory to derive a theoretical link between the elastic constant of fat crystal networks and the structure of the network, using the fractal dimension of the network as a mathematical indicator of the structure. Many attempts have been made to relate the macroscopic properties of fat crystal networks to the lipid composition (triglycerides) and the polymeric nature of the network, but these have not been successful. In this paper, we approach the problem from a microstructural perspective. The level of structure of a fat crystal network which most influences its macroscopic behavior is its microstructure, since it is this level of structure which is closest to the macroscopic world. The individual microstructures in fat crystal networks can vary from a diameter of 80 μm to above 120 μm, depending on the system (microstructures in cocoa butter are shown in Fig. 1), and are therefore closer to the macroscopic level than the structure of the triglyceride molecules or the crystalline units of particular polymorphs. No level of structural “building blocks” larger than the microstructural level has been observed in fat crystal networks, although much evidence of the existence of “clusters” or microstructures of the order of 1 μm have been published, initially by a group at Unilever Research Laboratory in the Netherlands [5–7]. In order to develop our theory, it is first necessary to introduce the various levels of structure of
Structural view – a colloidal gel?
Fat crystal networks display statistical self-similarity and scaling behavior characteristic of stochastic fractal systems.
Statistical Self similarity – you guess!
Self-similarity?

$D_b = 1.60$
Scaling Behavior and Fractional Dimensionality

Scaling behavior $G \sim \Phi^\mu$

Scaling behavior $N \sim L^D$

$r^2=0.88$

$D=2.45$

$r^2=0.994$

$D=2.01 (0.06)$
$\xi \sim \Phi^\mu$
\[ \xi \sim t^{1/D} \]

\[ \text{Log}_{10} \text{ Diameter (\(\mu m\))} \]

\[ \begin{align*}
\text{Log}_{10} \text{ Time (seconds)} & \\
A & \\
slope = 0.67 \pm 0.009 \\
D & = 1.49 \pm 0.019 \\
\end{align*} \]

\[ \begin{align*}
\text{Log}_{10} \text{ Time (seconds)} & \\
B & \\
slope = 0.72 \pm 0.055 \\
D & = 1.40 \pm 0.106 \\
\end{align*} \]

SFC linear with time

\[ \text{Milkfat Spherulites at 20}^\circ\text{C} \]

for \( M \sim t \)

Batte and Marangoni, 2005, Crystal Growth and Design 5: 1703-1705
Fractal Structural-mechanical model
The view
Weak-link Theory - Fat Crystal Networks

Developed for colloidal gels and adapted to fat crystal networks:

\[ G' \sim \Phi^\mu \sim \lambda \Phi^{1/(d-D)} \]

\( G' \) = dynamic shear elastic modulus (storage modulus)
\( \lambda \) = constant which depends on particle properties and particle-particle interactions
\( \Phi \) = solids’ volume fraction of fat sample

Narine and Marangoni, 1999, PRE 59:1908
Fractal dimension - rheology

\[ G' = \lambda \left( \frac{SFC}{100} \right)^\mu \]

\[ \ln G' = \ln \lambda + \mu \ln \left( \frac{SFC}{100} \right) \]
Effect of $D$ on the Elastic Modulus

![Graph showing the effect of $D$ on the Elastic Modulus]
Relationship to Large Deformation Rheological Behavior?

![Graph showing the relationship between E' (MPa) and yield force (g force). The correlation coefficient r^2 is 0.80.](image)
Effects of shear on $D_r$ (AMF)

\[ D_{\text{max}} - D = \frac{\beta}{\text{SR}} \]

\[ \ln \frac{\lambda}{\lambda_o} = -\alpha (\text{SR}) \]
Crystallization behavior and structure

\[ D = D^* + \beta \ln J \]

Marangoni and McGauley, 2003, Crystal Growth and Design 3, 95
\[ G' = \lambda \Phi \frac{1}{d-D} = \lambda \Phi \frac{1}{d-D^* - \beta \ln J} \]
Thermomechanical Method for the Determination of the Rheology Fractal Dimension
AMF G' vs Temperature

Temperature (deg Celcius)
G' (Pa)
$r^2 = 0.996$
$D = 2.68$

$Dilution$
$r^2 = 0.938$
$D = 2.70$

$Thermo$
$r^2 = 0.996$
$D = 2.68$
CB SFC vs. Temperature vs.

Temperature (deg Celcius)

SFC (%)
Dilution
\[ r^2 = 0.92 \]
\[ D = 2.43 \]

Thermo
\[ r^2 = 0.98 \]
\[ D = 2.40 \]
Structure-mechanical model
Thermodynamic arguments

\[ E = \frac{6\delta}{a\varepsilon^*} \Phi \frac{1}{3-D} = \frac{A}{2\pi a\varepsilon^* d_o^2} \Phi \frac{1}{d-D} \]

\[ G = \frac{1}{3} E \]

Marangoni and Rogers, 2003, Appl. Phys. Lett. 82, 3239
The Yield Stress (Compression)

\[ \sigma^* = E \cdot \varepsilon^* \]

\[ \sigma^* = \frac{6\delta}{\Phi} \frac{1}{\alpha^{3-D}} \]

Marangoni and Rogers, 2003, Appl. Phys. Lett. 82, 3239
Global indicator of functionality!

- Yield Stress is a function of SFC, structure and intercrystalline interactions
- Easy to determine precisely
- Possible to deconvolve into SFC, structure and interaction effects
Model simulations

(a) $a=200\,\text{nm}$
$D=2.8$
$\delta\, (\text{J}\,\text{m}^{-2}) \rightarrow \text{var}$
$0.005 \quad 0.03 \quad 0.01$
$\sigma^*\, (\text{Pa})$

(b) $\delta=0.01\,\text{J}\,\text{m}^{-2}$
$D=2.8$
$a\, (\text{nm}) \rightarrow \text{var}$
$100 \quad 200 \quad 500$
$\sigma^*\, (\text{Pa})$

(c) $\delta=0.01\,\text{J}\,\text{m}^{-2}$
$a=200\,\text{nm}$
$D \rightarrow \text{var}$
$2.7 \quad 2.75 \quad 2.8$
$\sigma^*\, (\text{Pa})$
\( \delta = 0.01 \text{ J m}^{-2} \)
\( a = 130 \text{ nm} \)
\( D = 2.79 \)

\( \delta = 0.01 \text{ J m}^{-2} \)
\( a = 810 \text{ nm} \)
\( D = 2.67 \)

\( \delta = 0.01 \text{ J m}^{-2} \)
\( a = 740 \text{ nm} \)
\( D = 2.69 \)
What about intermolecular interactions?
Van der Waal Interactions

• Origen: permanent and induced dipoles

• Contribution to the van der Waals Interactions

  • Keesom: \( P-D \) \( \leftrightarrow \) \( P-D \)
  • Debye: \( P-D \) \( \leftrightarrow \) \( I-D \)
  • London: \( I-D \) \( \leftrightarrow \) \( I-D \) also called “Dispersion”
Hamaker Coefficient

$$E_{vdW}(r) = c \frac{A}{r^m}$$

<table>
<thead>
<tr>
<th>Configuration</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule: point to point</td>
<td>6</td>
</tr>
<tr>
<td>Two-plane parallel bodies</td>
<td>2</td>
</tr>
<tr>
<td>Two spherical particles</td>
<td>1</td>
</tr>
</tbody>
</table>

Hamaker coefficient = property of the material

Strength of the material via van der Waals interactions
Lifshitz theory

Effective medium theory

Measured dielectric response of the material for the whole electromagnetic spectrum

\[ A = \frac{3 \, K \, T}{2} \sum \left( \frac{(\varepsilon_1 - \varepsilon_3)}{(\varepsilon_1 + \varepsilon_3)} \right) \left( \frac{(\varepsilon_2 - \varepsilon_3)}{(\varepsilon_2 + \varepsilon_3)} \right) \text{Rel}(r) \]

- \( K \) Boltzmann’s constant
- \( T \) Temperature (absolute)
- \( \varepsilon \) dielectric permittivity

\[ A = A_{\text{(v=0)}} + A_{\text{MIC (rot.)}} + A_{\text{IR (vib.)}} + A_{\text{UV (elec.)}} \]
Approximation to Lifshitz Theory
Ignoring the Retarded Potential

Intermolecular and Surface Forces, Israelachvili

\[
A = \frac{3}{4} KT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right)^2 + \frac{3 h \nu_e}{16 \sqrt{2}} \frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}}
\]

K  Boltzmann’s constant
h  Planck’s constant
T  Temperature (absolute)
\( \varepsilon \)  dielectric permittivity
n  index of refraction
\( \nu \)  electronic absorption frequency in the UV region = 3 \times 10^{15} \text{ s}^{-1}

Index 1 and 3 are for “particle” and “medium” respectively
“A” obtained from the approximation to LT

\[ A = \frac{3}{4} KT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \left( n_1^2 - n_3^2 \right)^2 \left( n_1^2 + n_3^2 \right)^{3/2} \]

<table>
<thead>
<tr>
<th>A (J)</th>
<th>( \varepsilon ) (_{\text{FHCO}} )</th>
<th>( \varepsilon ) (_{\text{HOSO}} )</th>
<th>Lab.</th>
<th>( n_{\text{FHCO}} ) ((\lambda=589\text{nm}))</th>
<th>( n_{\text{HOSO}} ) ((\lambda=589\text{nm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.35 (10^{-22})</td>
<td>3.55</td>
<td>2.38</td>
<td>U o C</td>
<td>1.506737</td>
<td>1.466133</td>
</tr>
<tr>
<td>5.70 (10^{-22})</td>
<td>1.68(^{\text{Est.}})</td>
<td>2.65</td>
<td>U o W</td>
<td>1.506737</td>
<td>1.466133</td>
</tr>
<tr>
<td>4.43 (10^{-22})</td>
<td>3.55</td>
<td>2.92</td>
<td>U o Win</td>
<td>1.506737</td>
<td>1.466133</td>
</tr>
</tbody>
</table>
Dielectric Constant

Index of refraction

Measurements
OSCAR: Open Source Capacitance Analyzer

Parallel Plate capacitor device
Structural-mechanical fractal model

Marangoni and Rogers, 2003, Appl. Phys. Lett. 82, 3239
Narine and Marangoni, 1999, Phys. Rev. E 60, 6991
Fat Crystal Network Model

\[ G' = \lambda \phi^{\frac{1}{3-D}} = \frac{A}{6 a \pi \gamma d_0^2} \phi^{\frac{1}{3-D}} \]

<table>
<thead>
<tr>
<th>Variables</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda )</td>
<td>Experimental value, obtained from a ln ( G' ) vs. ln ( \Phi ) plot</td>
</tr>
<tr>
<td>( a )</td>
<td>diameter of particles</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Strain at the limit of linearity</td>
</tr>
<tr>
<td>( d_0 )</td>
<td>separation between the “flocs”, ( d=0.165 \text{nm} ) (Israelachvili)</td>
</tr>
</tbody>
</table>

Hamaker Constant

SFC
Hamaker constant obtained from Fractal Model

Experimental values:
Temperature: 30°C
\( \varepsilon = 1.9 \times 10^{-4} \)
\( \lambda = 1.7 \times 10^7 \) Pa

<table>
<thead>
<tr>
<th>A (J)</th>
<th>( d_o ) (nm)</th>
<th>a (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.46 ( 10^{-22} )</td>
<td>0.2</td>
<td>110</td>
</tr>
<tr>
<td>2.44 ( 10^{-22} )</td>
<td>0.2</td>
<td>200</td>
</tr>
<tr>
<td>5.82 ( 10^{-22} )</td>
<td>0.2</td>
<td>240</td>
</tr>
</tbody>
</table>
## Comparison to previous work

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temp. (°C)</th>
<th>Refractive index</th>
<th>Permittivity</th>
<th>Hamaker Coefficient (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Media</td>
<td>Medium</td>
<td>Media</td>
</tr>
<tr>
<td>Peyronel and Marangoni</td>
<td>30</td>
<td>1.5067&lt;sup&gt;1&lt;/sup&gt;</td>
<td>1.4661&lt;sup&gt;3&lt;/sup&gt;</td>
<td>3.55&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Johansson and Bergenstahl</td>
<td>60*</td>
<td>1.45&lt;sup&gt;2&lt;/sup&gt;</td>
<td>1.4735&lt;sup&gt;4&lt;/sup&gt;</td>
<td>2&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Kloek</td>
<td>60*</td>
<td>1.56&lt;sup&gt;2&lt;/sup&gt;</td>
<td>1.4735&lt;sup&gt;4&lt;/sup&gt;</td>
<td>2&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

1<sup>Fully Hydrogenated Canola oil</sup>
2<sup>Tristearin</sup>
3<sup>High Oleic Sunflower Oil</sup>
4<sup>Soybean oil</sup>
5* infer from reference
Summary

\( A_{\text{fractal model}} \approx A_{\text{Lifshitz}} \)

\( A = 2 \times 10^{-22} \text{ J Tristearin in soybean oil} \). Johannson et al. (JAOCS, Vol.69,8,1992)
Interesterified fully hydrogenated stocks (high stearic acid) with high-oleic oils
<table>
<thead>
<tr>
<th>Major fatty acids</th>
<th>Carbon No.</th>
<th>Fully hydrogenated canola oil</th>
<th>High oleic sunflower oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic acid</td>
<td>16:0</td>
<td>8.8</td>
<td>5.1</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>18:0</td>
<td>88.0</td>
<td>5.9</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>18:1</td>
<td>0.08</td>
<td>76.8</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>18:2</td>
<td>0.03</td>
<td>8.0</td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>18:3</td>
<td>0.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Eicosanoic acid</td>
<td>20:0</td>
<td>1.9</td>
<td>0.0</td>
</tr>
</tbody>
</table>
**Interesterification of a binary mixture (50/50) of OOO and SSS**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>OOO + SSS</td>
<td><strong>OSO</strong> (12.5%)</td>
</tr>
<tr>
<td></td>
<td><strong>OOS / SOO</strong> (25%)</td>
</tr>
<tr>
<td></td>
<td><strong>OOO + SSS</strong> (25%)</td>
</tr>
<tr>
<td></td>
<td><strong>SSO / OSS</strong> (25%)</td>
</tr>
<tr>
<td></td>
<td><strong>SOS</strong> (12.5%)</td>
</tr>
</tbody>
</table>

**Sodium methoxide, Lipases**
Dramatic change in SFC-temperature profile
m = Slope of the Fisher-Turnbull plot, $\Delta H_f$ = (J/mol) enthalpy of fusion, $k_B =$ Boltzman’s constant ($1.38 \times 10^{-23}$ J/K), $V_m$ (m$^3$/mol) = MW/density, $T_f$ (K) = melting temperature

$$\delta = \left( \frac{3mk_B\Delta H^2_f}{16\pi(V_m^*)^2T^2_f} \right)^{1/3}$$

$$\sigma = \frac{6\delta}{\Phi^{3-D}}$$
\[ \sigma = \frac{6\delta}{\phi^{3-D}} \]

\[ \delta/a = 0.0286 \quad \text{~140nm} \quad -30\% \quad \text{~100nm} \]

\[ \delta/a = 0.020 \]

\[ E = 206 \text{ N} \quad \text{~30\%} \quad E = 114 \text{ N} \quad \text{~45\%} \]
Effects of shear

100sni, eq diam

100sni, sheared eq diam

Crystal length, nm

Size, nm

Frequency, %

Frequency, %
Thank You!