Properties of Lipids

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Properties of Lipids

Crystallization: Oils can be crystallized. The stages are *supercooling, nucleation, crystal growth and crystal maturation.*

Polymorphism: Fats can transform into solid form by forming different crystal structures.

Melting point: Melting is the transition from solid state to liquid state. It varies according to the oil type. The melting point can be changed by interesterification.

Density: Density can vary according to the fatty acid distribution of the oils and the minor components in their structure. Density is especially important in trade.

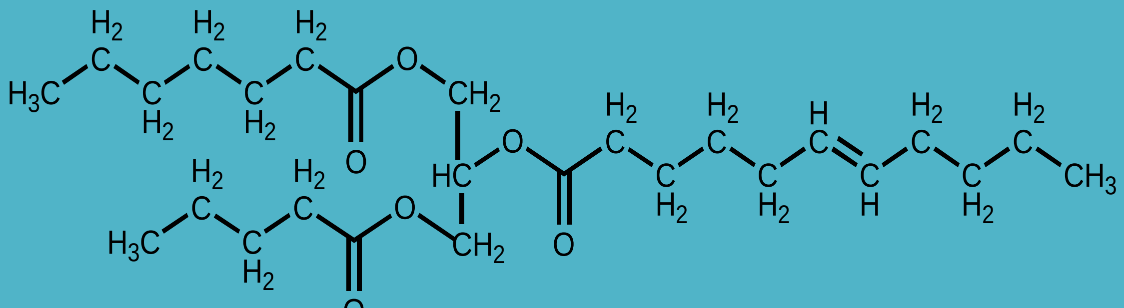
Viscosity: Varies according to the chemical properties of oils. Fluidity increases with temperature.

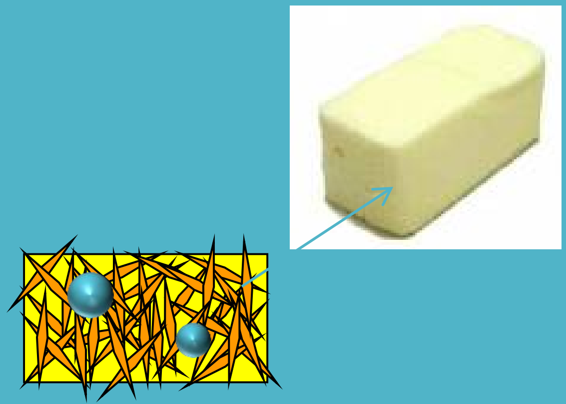
Refractive index: It is important in characterizing oils.

Lipids: Physical Properties

Melting and Crystallization Behavior

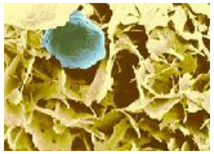
- Melting Point
- Crystallization Point
- Solid Fat Content *versus* Temperature
- Crystal Structure (Polymorphic form)
- Crystal Morphology (Size and Shape)

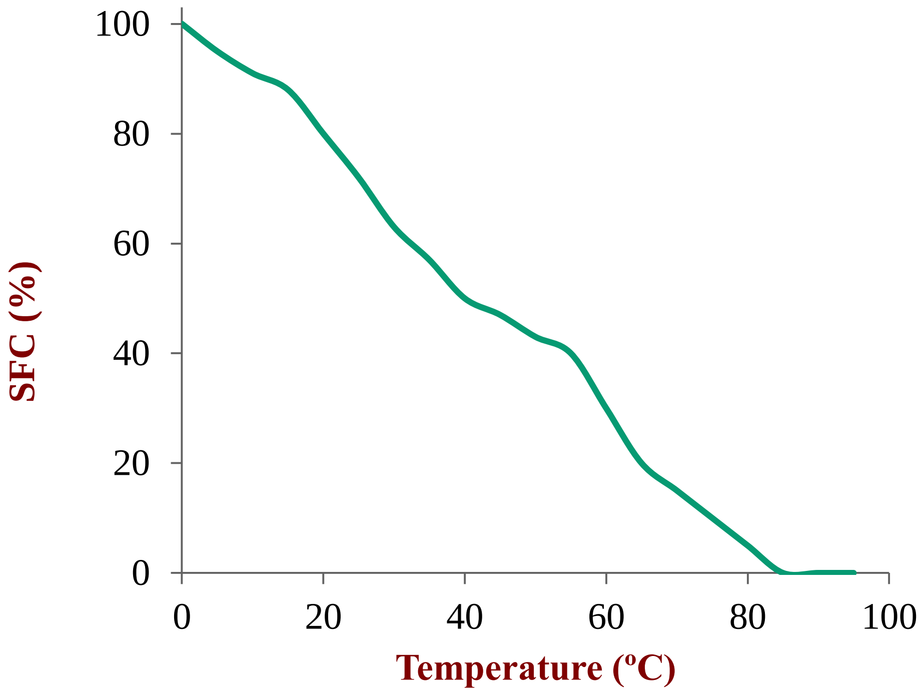




Physical Properties of Lipids:
Solid Fat Content

The melting profile (***Solid Fat Content vs. Temperature***) determines the specific application of the edible oil/fat thus is an important quality control parameter for both the suppliers and end users, as well as for the purpose of product development.

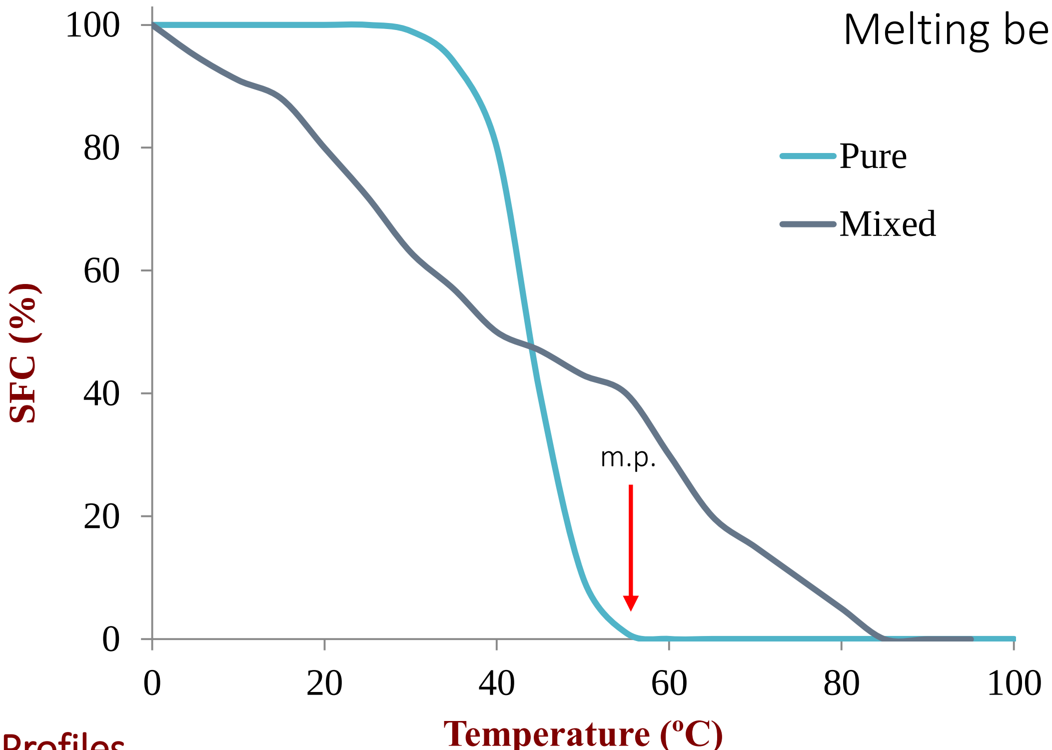




SFC Profile – The SFC-temperature profile of a particular fat is determined by fatty acid composition

Physical Properties of Lipids:
Solid Fat Content (SFC) Profile

Melting behavior



DSC

NMR

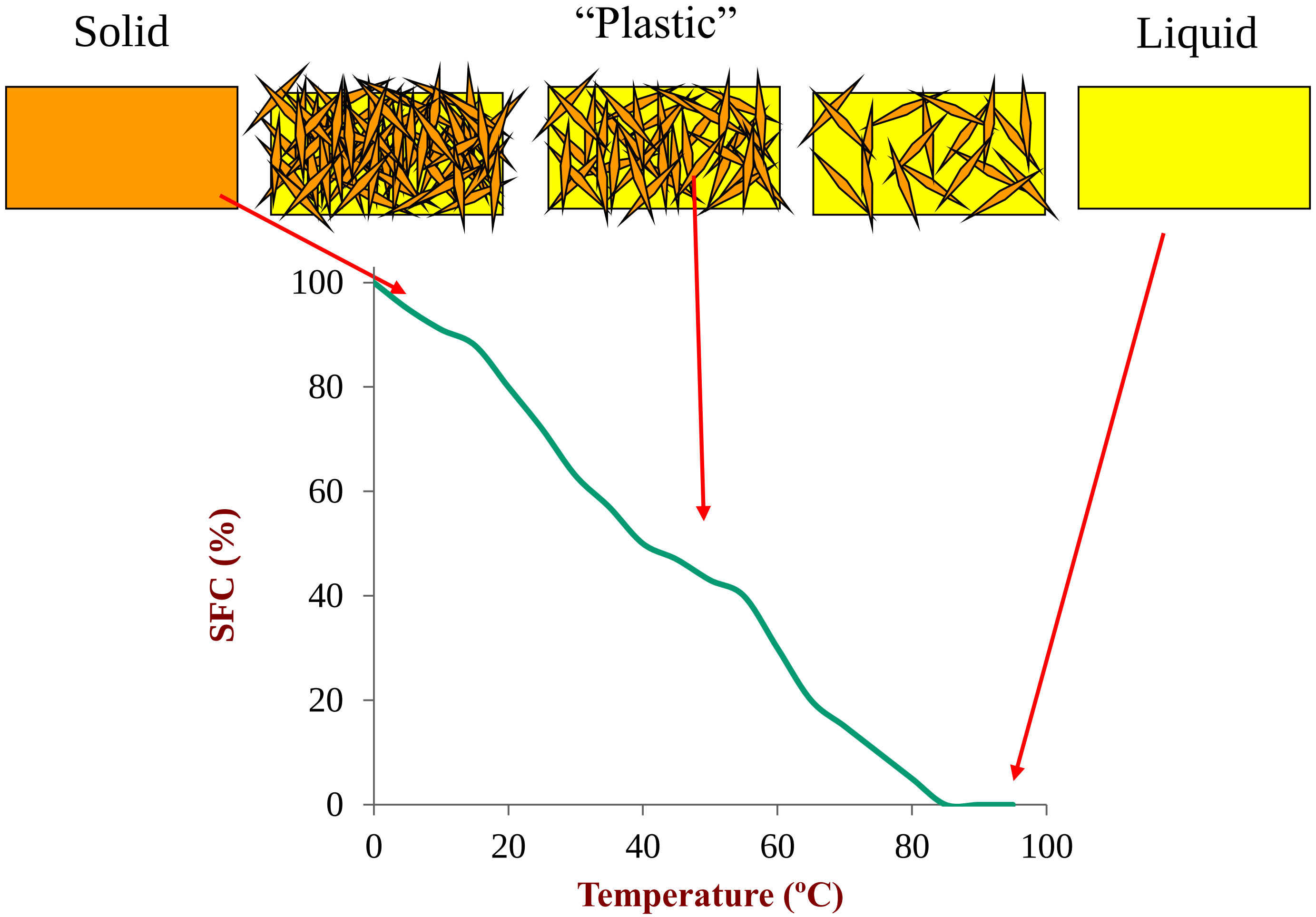
SFC-temperature Profiles

- The SFC-T profile of a pure triacylglycerol has a sharp melting point.
- The SFC-T profile of a mixed fat depends on the melting points of the individual components, as well as the solubility of high melting components in low melting components.
- The SFC-T profile of an edible fat is determined by its fatty acid composition
- The SFC-T profile can be measured by density, **Differential scanning calorimetry** (DSC), or Nuclear magnetic resonance (NMR) measurements

Physical Properties of Lipids:

SFC and Plasticity

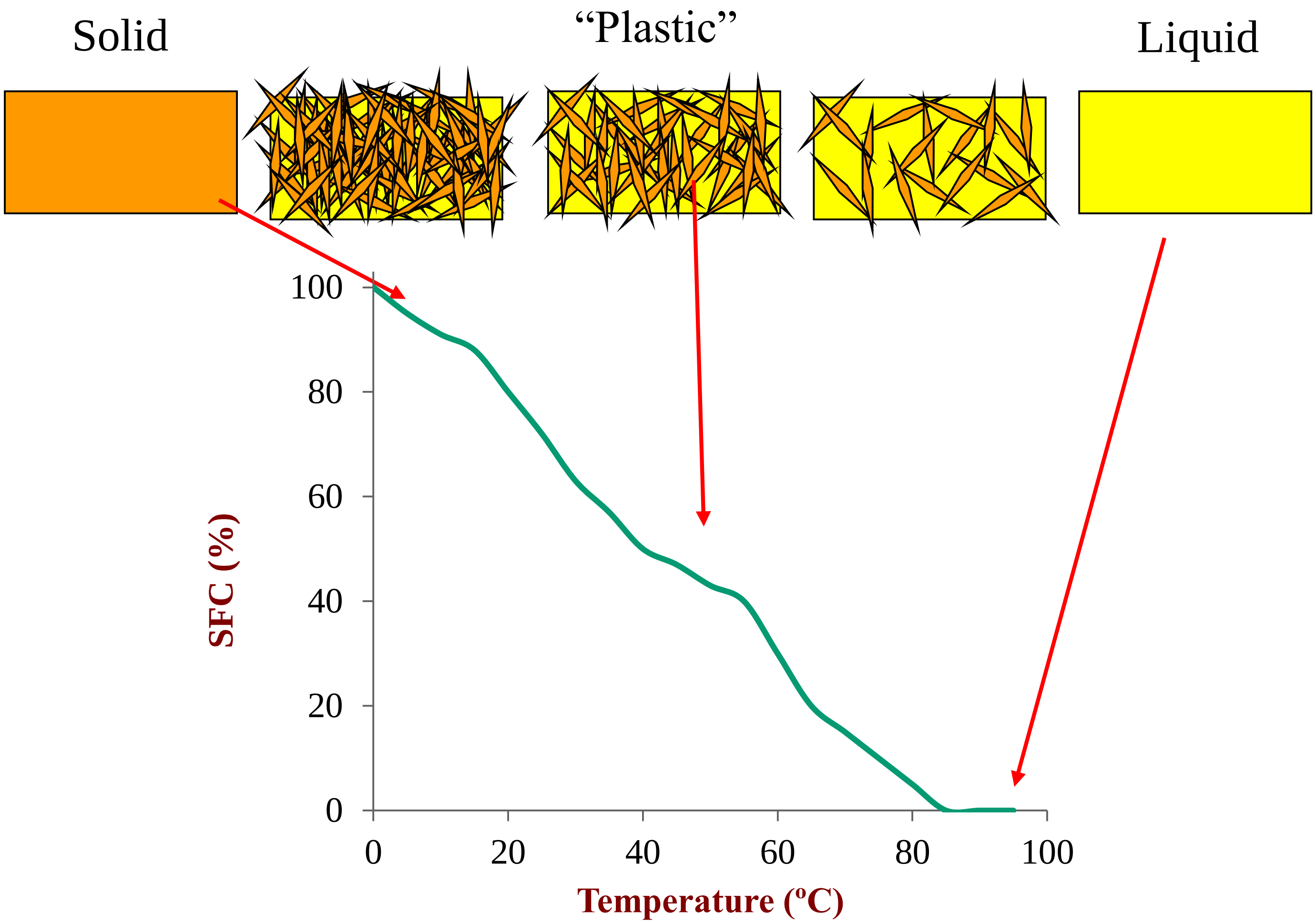
SFC curves, to a large extent, determine plastic behaviour



The plasticity of fat is the capacity to keep its shape yet can be molded or shaped by applying light pressure. It decides spreadability of fats. It is far foremost characteristic to consider when selecting a fat to be used in the baked products.

Physical Properties of Lipids:
SFC and Plasticity

SFC curves, to a large extent, determine plastic behaviour



Temperature affects plasticity, hard fats, for example, butter turning out to be soft and extra spreadable while warmed, even as chilled butter has very little or no plasticity. Usually, the unsaturation of fat increases its plasticity.

Melting Point: Saturated Fatty Acids

The melting point of fats varies according to the fatty acid (chain length, double bond number and isomer type) in their structure.

Short name	Common name	Systematic name	MW	MP (°C)	Formula
4:0	Butyric	Butanoic acid	88.11	-4.5	$CH_3(CH_2)_2COOH$
6:0	Caproic	Hexanoic	116.16	-2.0	$CH_3(CH_2)_4COOH$
8:0	Caprylic	Octanoic	144.21	16.5	$CH_3(CH_2)_6COOH$
10:0	Capric	Decanoic	172.27	31.5	$CH_3(CH_2)_8COOH$
12:0	Lauric	Dodecanoic	200.32	44.0	$CH_3(CH_2)_{10}COOH$
14:0	Myristic	Tetradecanoic	228.38	58.0	$CH_3(CH_2)_{12}COOH$
16:0	Palmitic	Hexadecanoic	256.43	63.0	$CH_3(CH_2)_{14}COOH$
18:0	Stearic	Octadecanoic	284.48	71.0	$CH_3(CH_2)_{16}COOH$
20:0	Arachidic	Eicosanoic	312.54	77.0	$CH_3(CH_2)_{18}COOH$

Melting point increases as the molecular weight of the fatty acids increases

Melting Point: Unsaturated Fatty Acids

Short name	Common name	Systematic name		MW	MP (°C)	Formula
16:1	Palmitoleic	Cis-9-hexadecenoic acid	ω7	254.4	1	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$
18:1	Oleic	Cis 9-octadecenoic	ω9	282.47	16.3	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
18:1	Elaidic	Trans 9-Octadecenoic	ω9	282.47	45.0	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
18:2	Linoleic	Cis 9, 12-Octadecadienoic	ω6	280.45	-5.0	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
18:3	α-Linolenic	Cis 9,12,15-Octadecatrienoic	ω3	278.44	-11.3	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
18:3	γ-Linolenic	6,9,12-octadecatrienoic	ω6			$CH_3(CH_2)_3(CH_2CH=CH)_3(CH_2)_4COOH$
20:4	Arachidonic	5,8,11,14-Eicosatetraenoic	ω6	304.47	-49.5	$CH_3(CH_2)_3(CH_2CH=CH)_4(CH_2)_3COOH$
20:5	EPA	5,8,11,14,17-Eicosapentaenoic	ω3		-54.4	
22:6	DHA	4,7,10,13,16,19-Docosahexaenoic	ω3		-44.5	

Melting point decreases as number of double bonds increases

Modifying Melting Behavior

Strategies to Modify Lipid Melting Behavior

Choice of Lipid Source

- Select a lipid source with the appropriate melting behavior

Blending

- Blend lipids from different sources

Fractionation

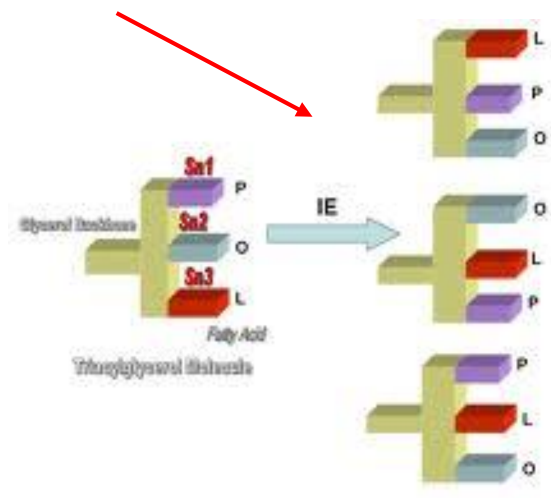
- Separate a lipid into different melting fractions

Inter-esterification

- Change the position of the fatty acids on the glycerol backbones

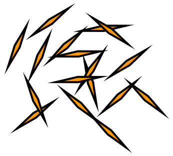
Hydrogenation

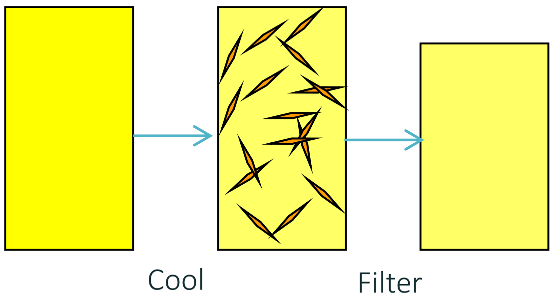
- Decrease the degree of unsaturation of fatty acids



Winterization

To remove **high melting TAGs** from liquid oils, thus preventing cloudiness at refrigeration temperatures (*i.e.* salad oils)





Two-step process

1. Crystallisation at low temperature i.e. 5°C

Slowly cooling at controlled rate

Gentle agitation

Gives large separable crystals

2. Filtration

Separate liquid oil from solid crystal cake using filter

Fractionation: General

- **Fractionation**
- To separate fats into high & low melting point fractions
- Similar process to *Winterization*, but this term is usually reserved for more saturated fats, *e.g.*, animal fats, palm oil, & palm kernel

  Can produce 2 or more fractions

Palm oil fractionation

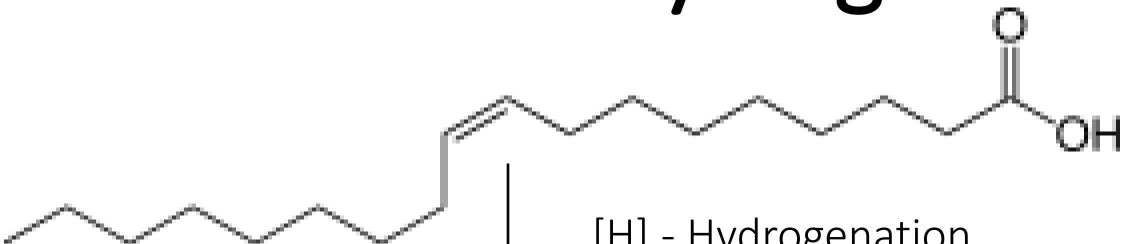
Low melting fraction (palm olein) – cooking/salad oil

High melting fraction (palm stearin) – shortening (frying oil) or margarine

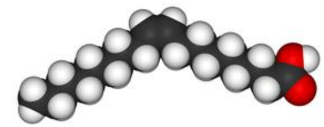
Milk fat fractionation

High melting, medium melting, low melting fraction (spreadable butter)

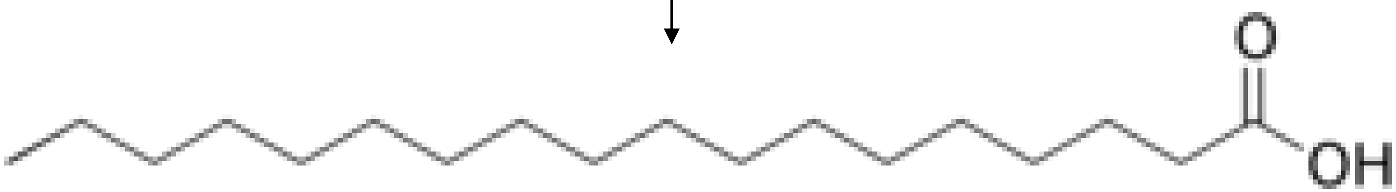
Lipid Structure: Hydrogenation



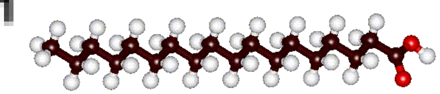
Oleic acid



[H] - Hydrogenation

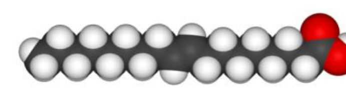


Stearic acid



But, as a minor product…

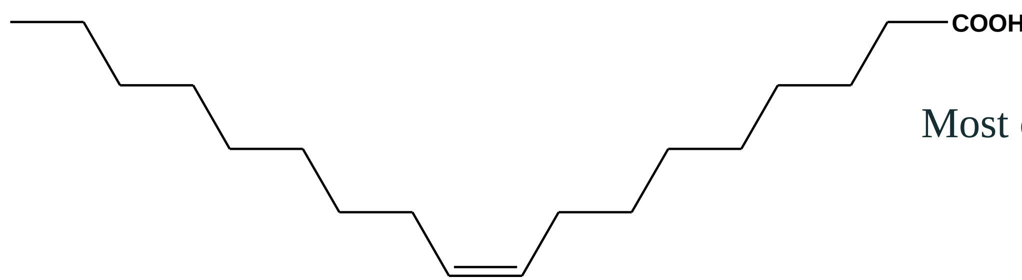
Eladic acid



A trans-fatty acid

Health problems!

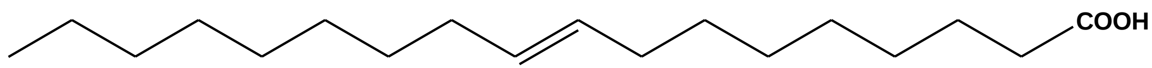
Lipid Structure: Trans *versus* Cis Forms



Most common in nature

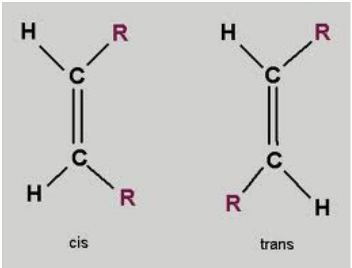
cis-9-octadecenoic acid (oleic acid)

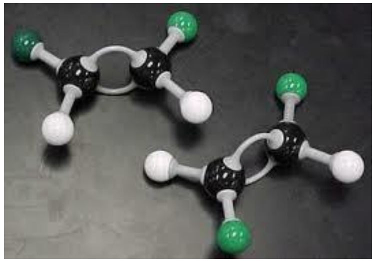
Occurs during processing



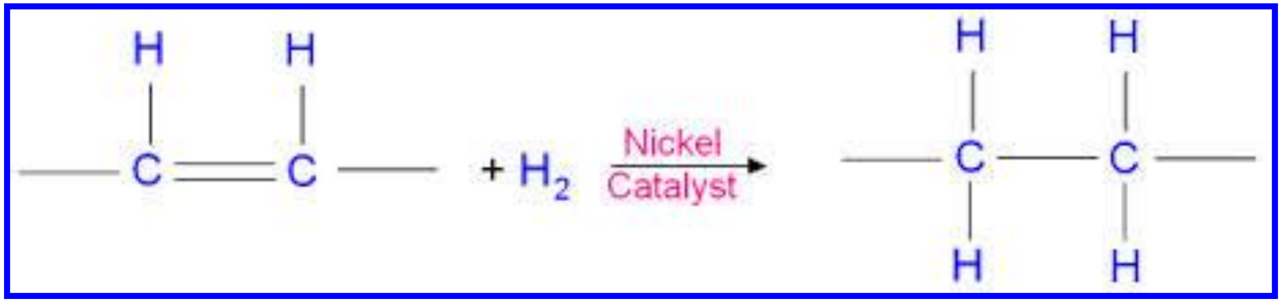
trans-9-octadecenoic acid (elaidic acid)

Practical Importance: Trans-fatty acids have a higher melting point than cis-fatty acids, have greater solidity, and are less prone to lipid oxidation

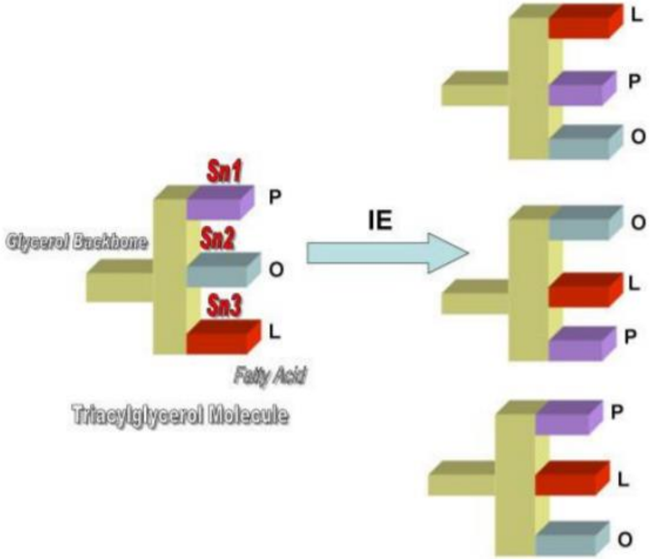




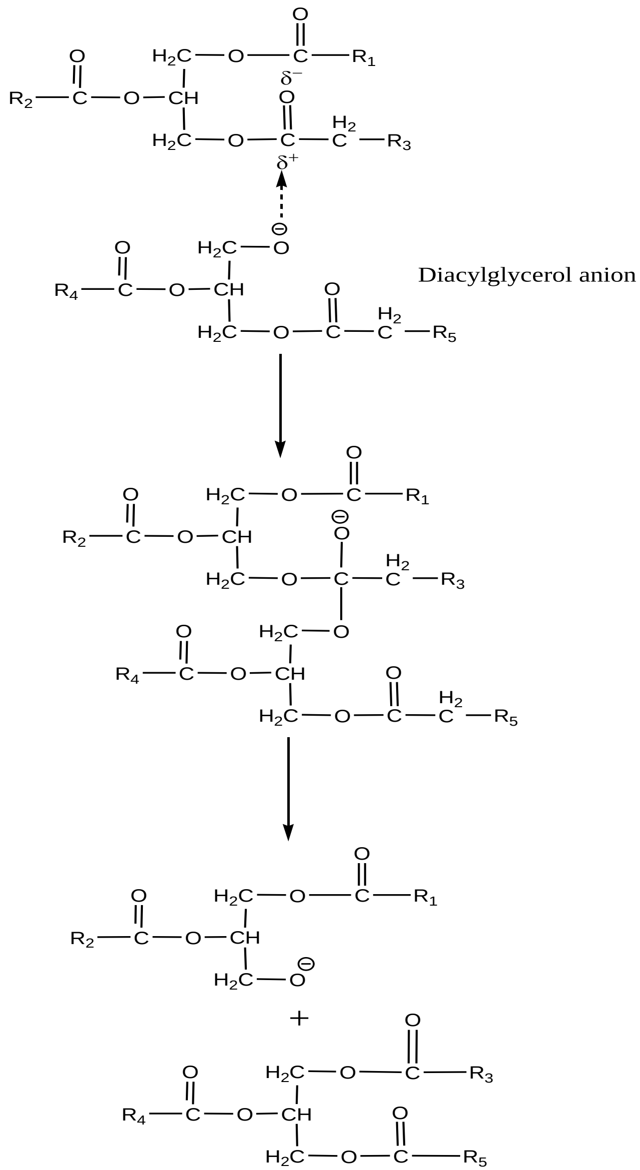
Hydrogenation: In the presence of a suitable catalyst (eg nickel), saturated fat can be formed by adding hydrogen to the double bond in the unsaturated fatty acid. This reaction forms the basis of margarine production.



Interesterification: interesterification is a process that rearranges the fatty acids of a fat product, typically a mixture of triglyceride. The physical properties of oils can be changed by this. High temperature alkali or low temperature Na-methylate is used in the process. It is the intramolecular or intermolecular change of the location of acyl groups in the structure of triglycerides.



Interesterification: Fatty Acid Rearrangement



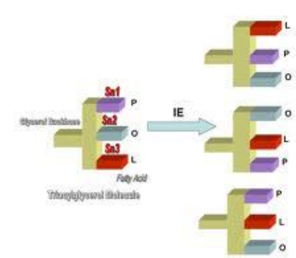
XXX + YYY

↓

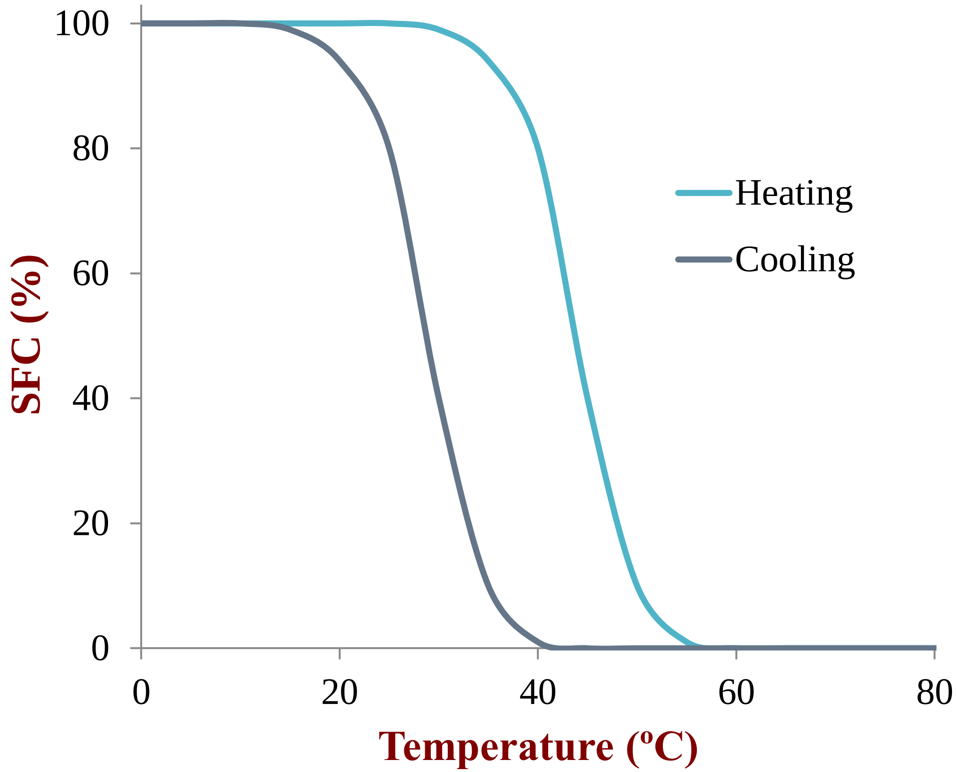
XXY + XYY + XYX + YXY + XXX + YYY

Process rearranges fatty acids on triacylglycerol:

- No change in saturated fatty acids
- No decrease in unsaturated fatty acids
- No formation of *trans* fatty acids
- Production of triacylglycerols that can be designed with different melting properties and nutritional attributes



Physical Properties of Lipids: Hysteresis and Supercooling

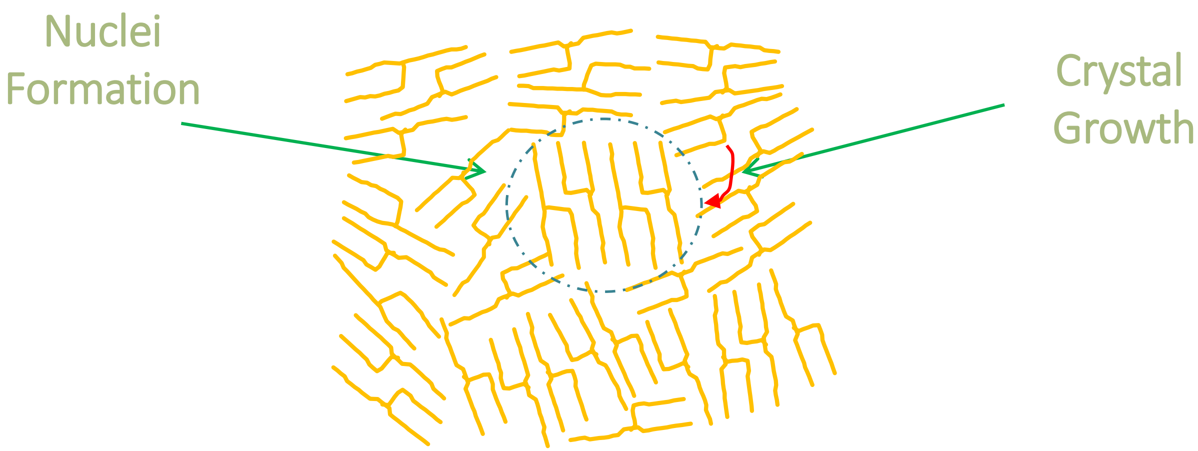


Supercooling, also known as undercooling, is the process of lowering the temperature of a liquid below its freezing point without it becoming a solid. It achieves this in the absence of a seed crystal or nucleus around which a crystal structure can form.

SFC Profile

- The SFC-temperature profile of a fat is usually different when they are cooled or heated, due to **supercooling** effects- The fat crystallizes at a lower temperature than it melts

Fat Crystallization: Kinetics



Liquid oil-to-solid fat transition:

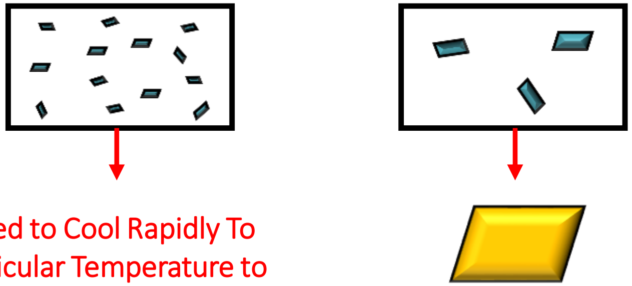
- **Supercooling -** Liquid oil can be cooled appreciably below its melting point before fat crystallization occurs
- **Nucleation –** Small clusters of oil molecules, called **nuclei**, need to form and be stable before fat crystals can grow
- **Growth –** Oil molecules join the existing fat crystal surfaces

Fat Crystallization: Fat Crystal Size

Factors Affecting Crystal Size

The size of the crystals formed depends on the relative rates of nucleation and growth.

- **Faster Nucleation Rate –** Many nuclei are initially formed that grow slowly, which results in the formation of many small crystals.
- **Faster Growth Rate –** A few nuclei are initially formed that grow quickly, which results in the formation of few large crystals

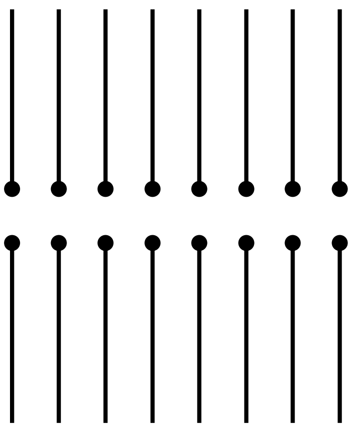


Need to Cool Rapidly To Particular Temperature to Avoid Large Crystals

Large fat crystals cause quality problems, such as "grittiness"

Physical Properties of Lipids:
Fatty Acid Polymorphism

A



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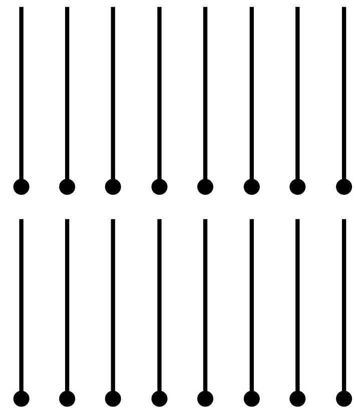

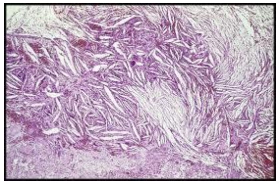

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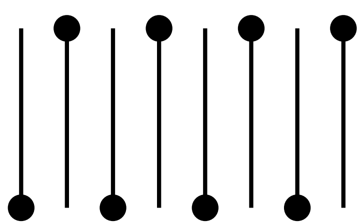

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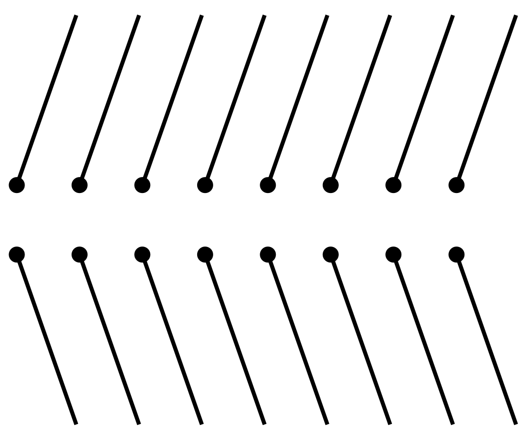
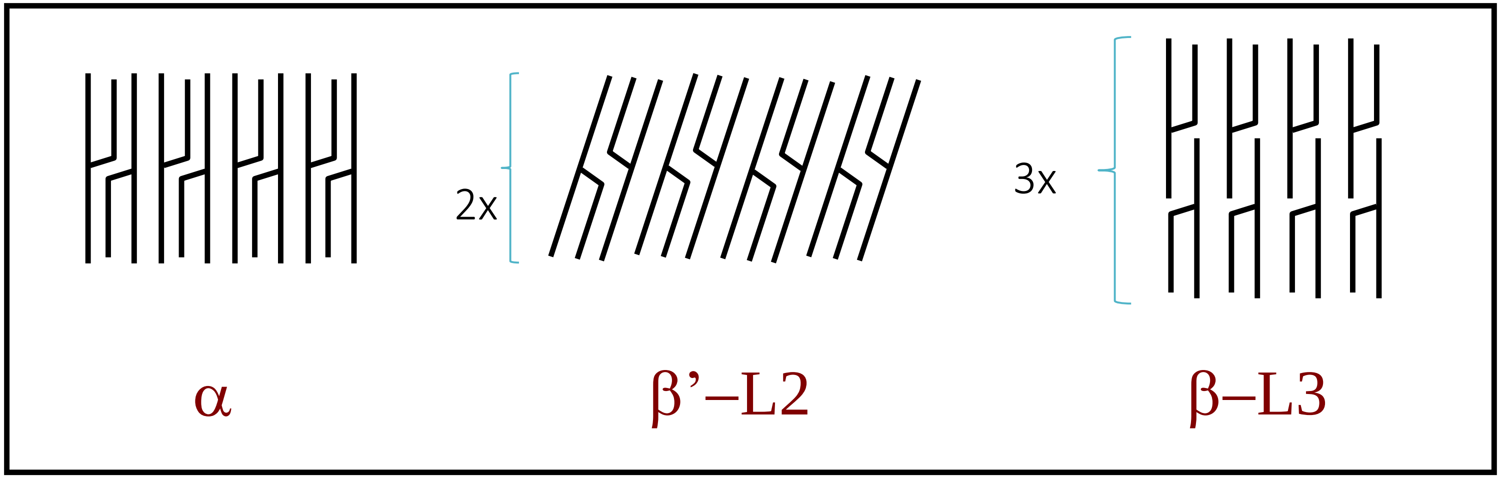


Polymorphism: Fatty acids can crystallize into a number of different molecular arrangements, forming crystals with different physicochemical properties (melting point, density, structure)

Physical Properties of Lipids:
Triacylglycerol polymorphism

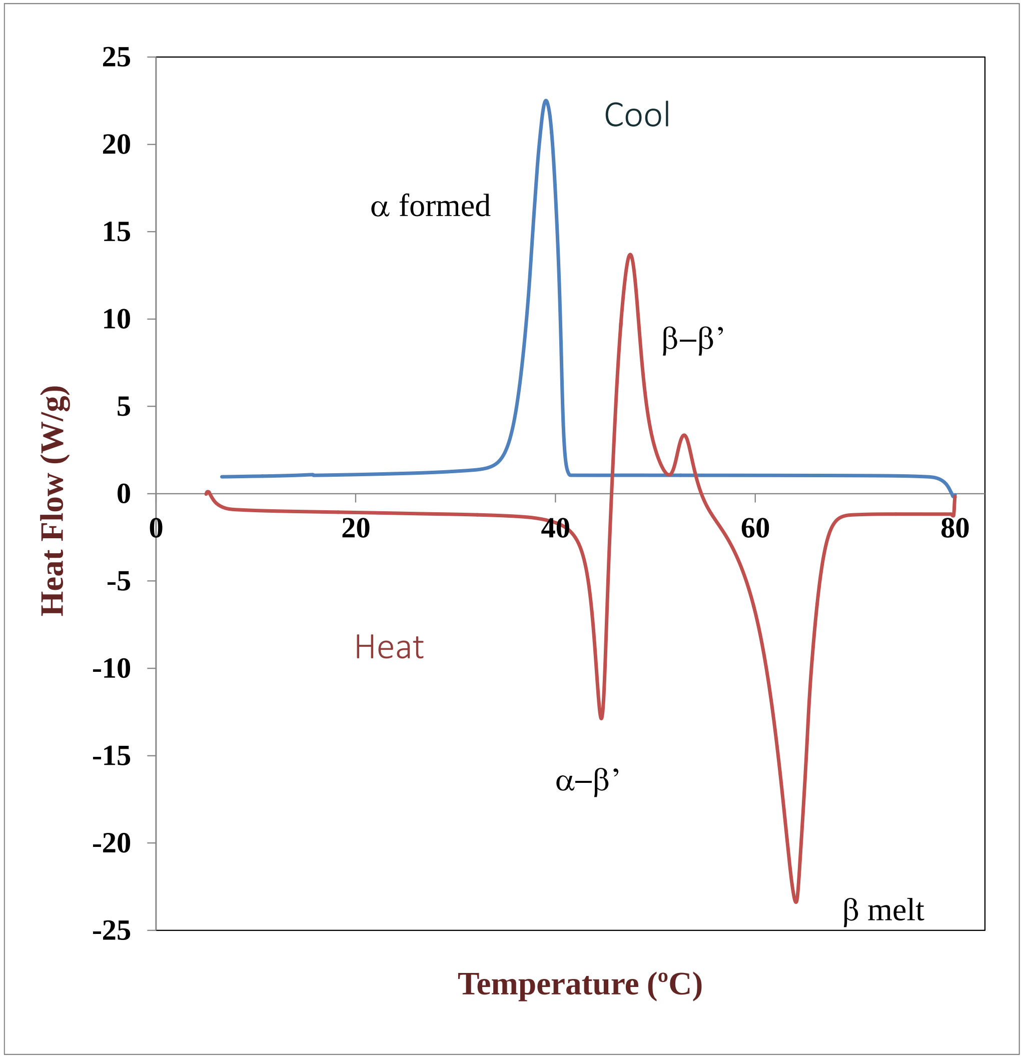
During the cooling of melted acylglycerols, one of the three polymorphic forms is yielded.



Polymorphism:

- Triacylglycerols can crystallize into a number of different molecular arrangements, forming crystals with different thermodynamic (free energies, enthalpies, entropies) and physicochemical properties (melting points, densities, structures)
- The crystals formed are given different symbols, e.g., α, β', β

Physical Properties of Lipids: Polymorphism



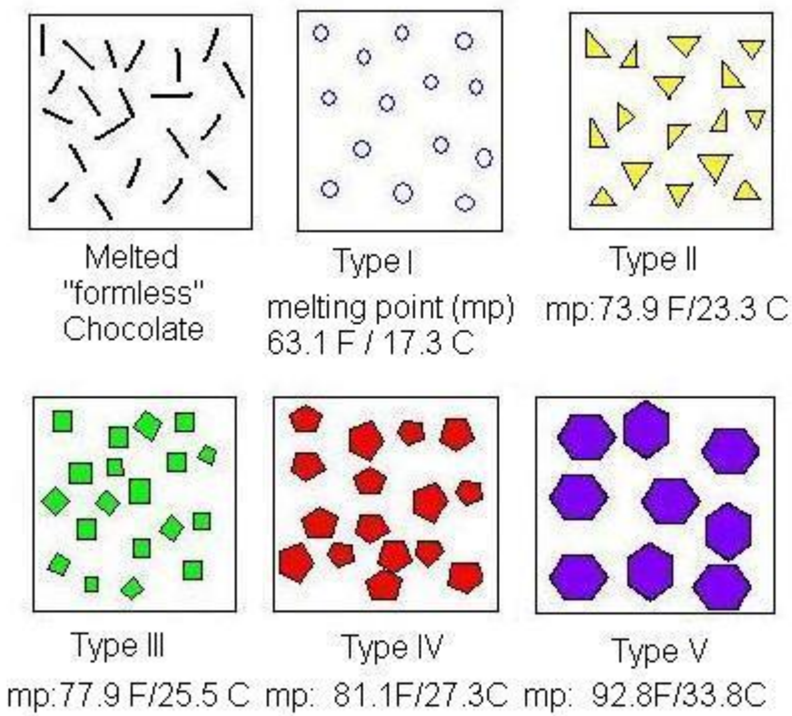
The α-form has the lowest melting point. This modification is transformed first into the β'-form upon heating and then into the β-form. The β-form is the most stable and hence, also has the highest melting point.

Polymorphism

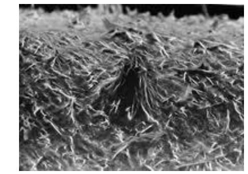
- DSC can be used to distinguish polymorphic forms

Physical Properties of Lipids: Polymorphism

In edible fats and oils mor than the three mentioned polymorphic forms can be present



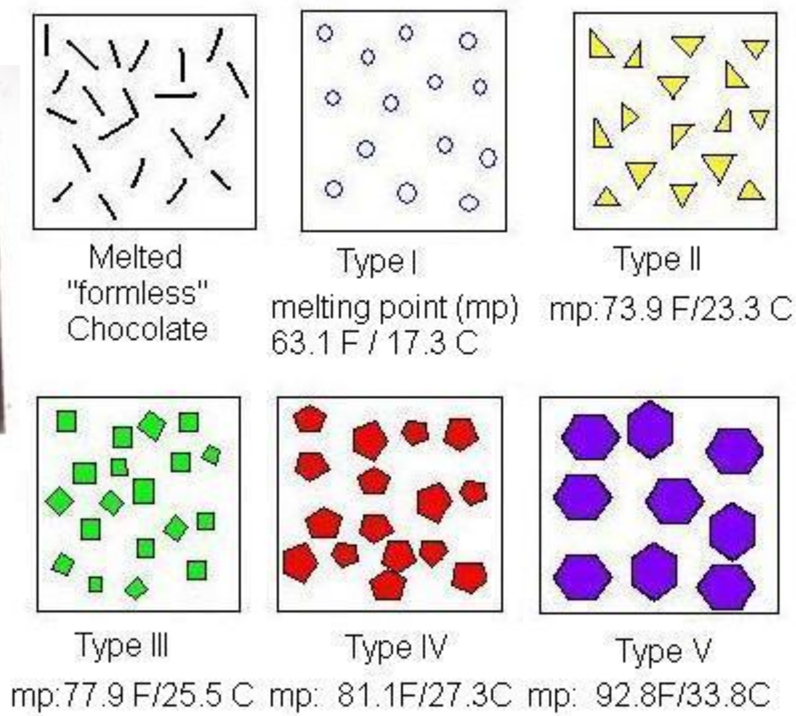
Polymorph Form V is the ideal form to achieve when working with chocolate.

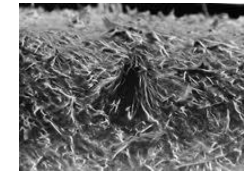


Polymorphism

- It is often important to control the polymorphic form of the fat crystals produced in a commercial food product, since this determines functionality such as appearance, texture ands stability.
- Elaborate procedures for controlling temperature-time profile are developed based on knowledge of different polymorphic phases

Physical Properties of Lipids:
Polymorphism_ Fat Bloom

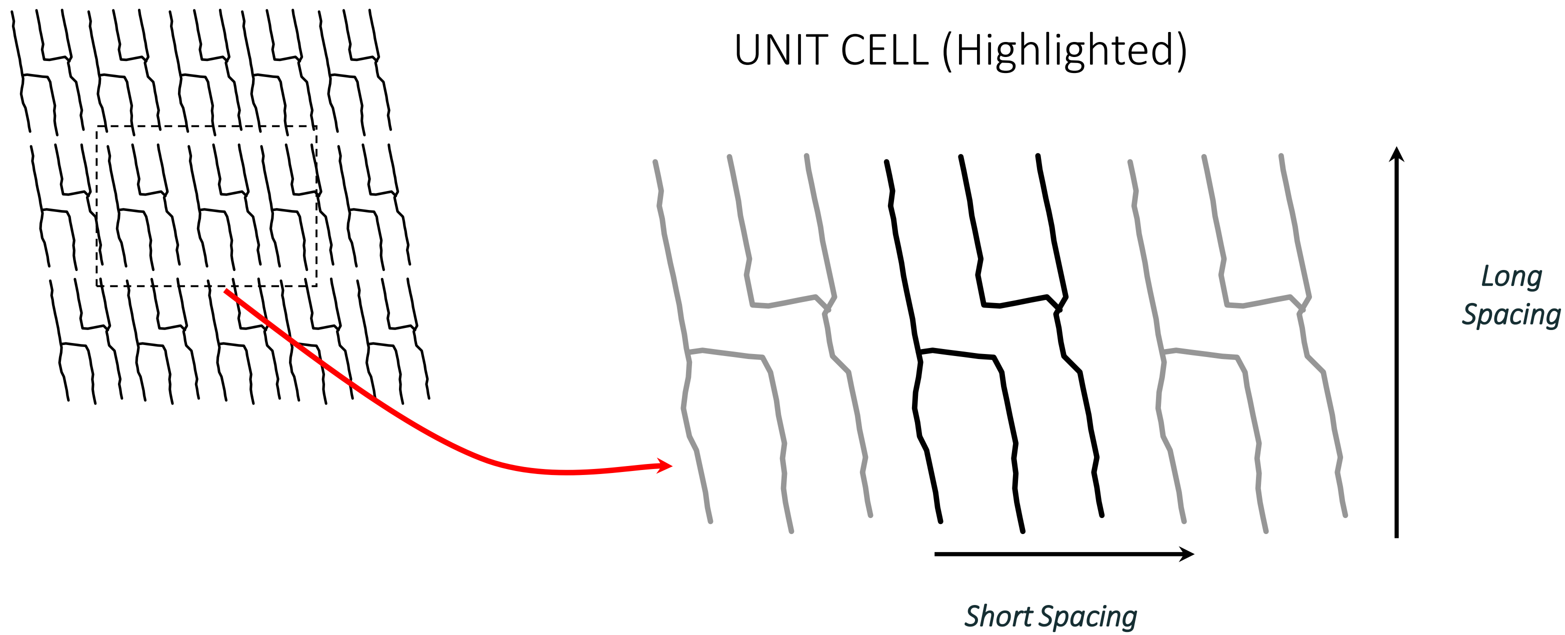




Polymorph Form V is the ideal form to achieve when working with chocolate.

Fat bloom is caused by a thin layer of fat crystals on the surface of the chocolate. The chocolate loses its gloss and a soft white layer appears. It is caused by changes in the fat crystals in the chocolate, due to extreme temperature fluctuations

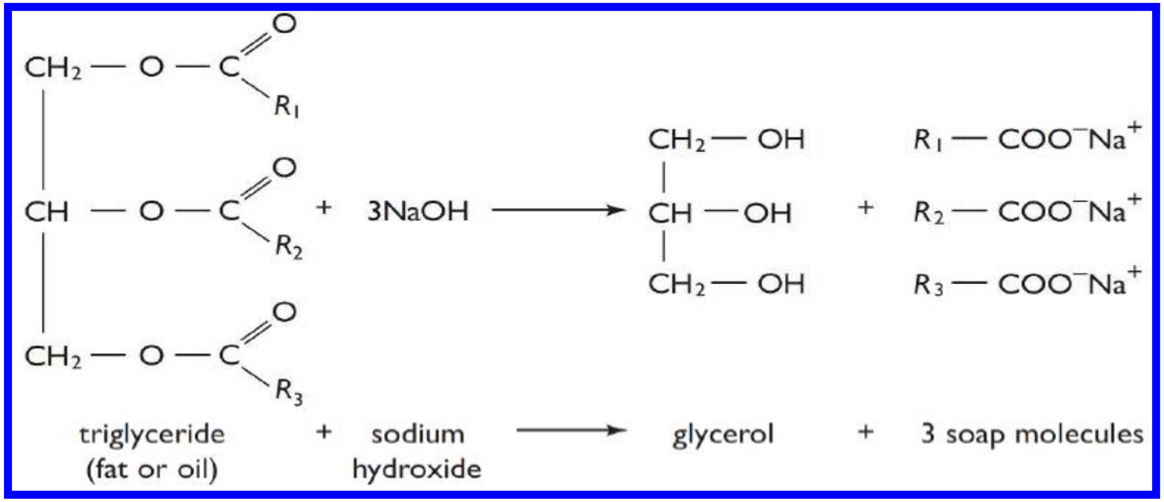
Physical Properties of Lipids:
Characterizing Fat Crystal Structure



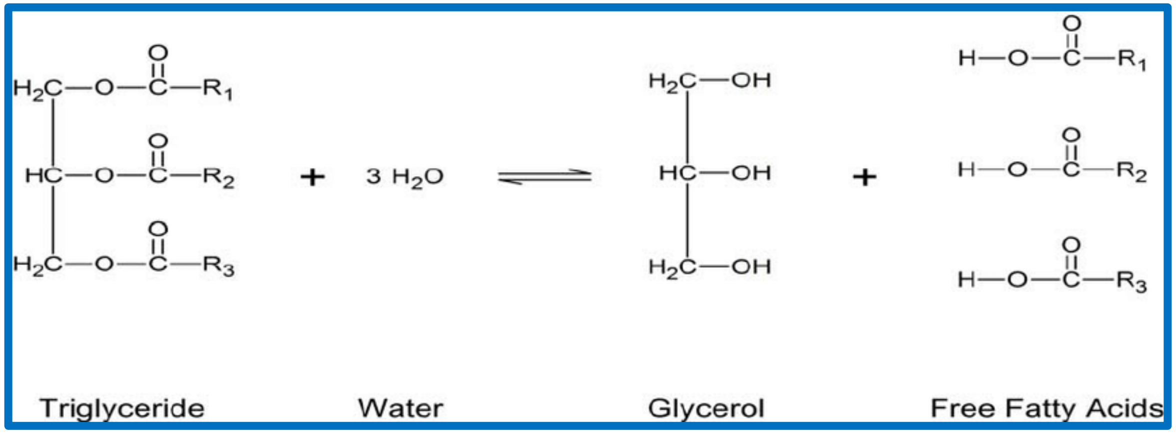
The crystal structure can be determined using a variety of methods, such as X-ray diffraction

Properties of Lipids

Saponification: Triglycerides can be hydrolyzed with alkalis. This is called saponification.

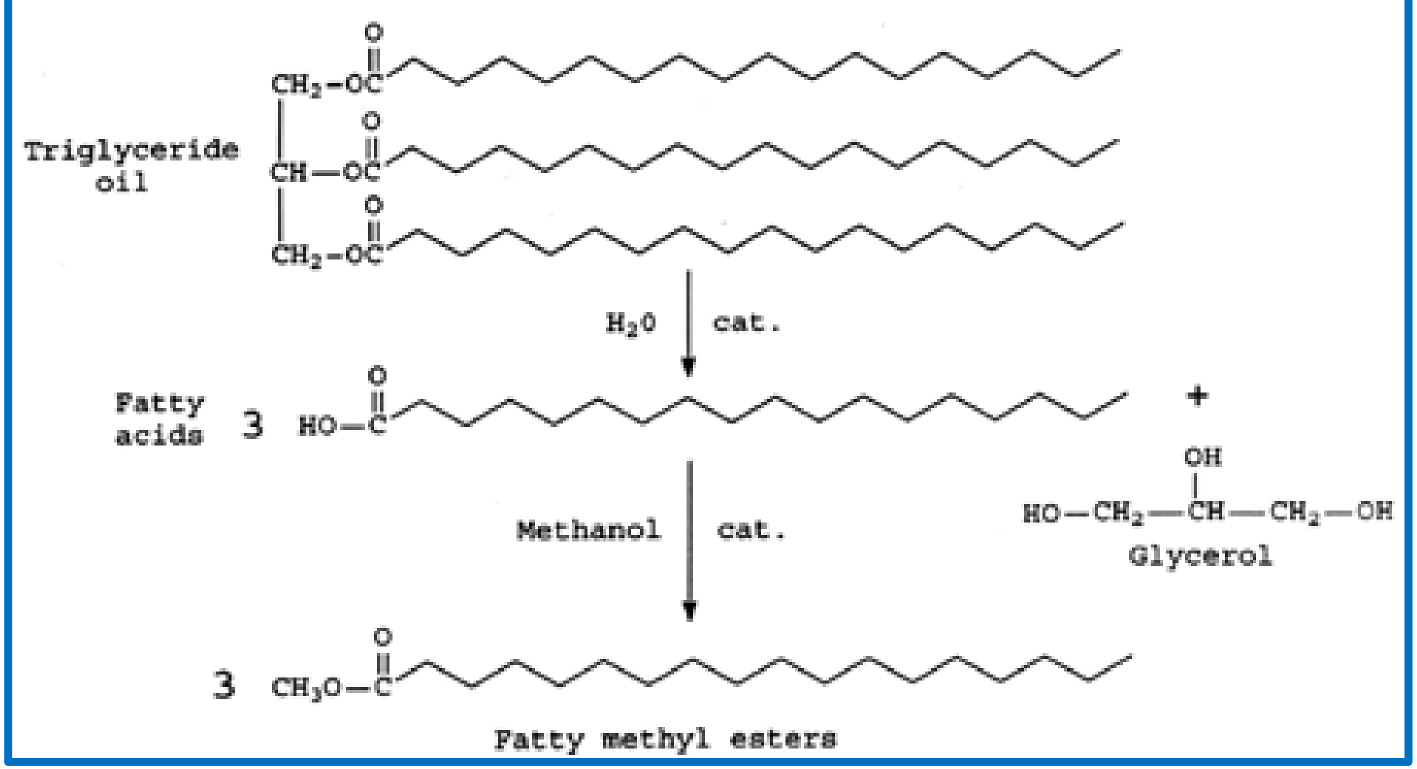


Hydrolysis: By enzymatic or acidic hydrolysis, triglycerides can be broken down into fatty acids and glycerol that form them.



Chemical Properties of Lipids

Methylation: It is important in determining fatty acid composition in triglycerides by Gas Chromatography. The fatty acid must be methylated (into its methyl ester form) for analysis. For this purpose, mainly Na-methylate is used.



<u>Halogenation:</u> A halogen such as iodine, bromine or chlorine can be added to the double bonds in the structure of an unsaturated oil. The number of double bonds in the structure of an oil can be determined by the iodine number. The more double bonds in the oil, the higher the iodine number.