Food Oils and Fats: Chemistry & Technology
Professor H N Mishra
Agricultural and Food Engineering Department
Indian Institute of Technology Kharagpur
Week 3: Edible Oils- Chemistry & Properties
Lecture 11: Engineering Properties of Edible Oils

NPTEL ONLINE CERTIFICATION COURSES

Food Oils and Fats: Chemistry and Technology

Professor H N Mishra

Agricultural and Food Engineering Department
Indian Institute of Technology Kharagpur

Module 03 : Edible Oils - Chemistry & Properties
Lecture 11 : Engineering Properties of Edible Oils

Concepts Covered

- Plant parts as a source of oil
  - ✓ Vegetable oils and fats
  - ✓ Oilseeds and nuts
  - ✓ Cereal oils
  - ✓ Fruit oils
  - ✓ Spice oils
- Utilisation pattern

Hello everybody. Namaskar. Now, we are in the module 3 of the course and in this module in the next 5 lectures, we will discuss about chemistry and properties of edible oil. So, in today's lecture that is the lecture 11, let us talk about engineering properties of edible oil. Here we will discuss physical properties, thermal properties, optical properties, rheological properties, plasticity and even crystallization and polymer version of edible oils and fats because these properties are very very important in using the fats and oils in food processing, deciding their usefulness even in deciding as well as in designing the equipment for handling for processing of these fruits and vegetables for these fats and oils in various food products.

Physical Properties of Edible Oils

- Oils constitute one of the essential components of balanced diet as good source of energy.
- The chemical and physical properties of oils are amongst the most important properties that determine the quality and help to describe the present condition of oils.
- Physical, chemical and nutritional properties of vegetable oils vary significantly depending on the type of fatty acids present in the oil.
- Vegetable oils also contain other compounds in minor amounts that affect their quality and nutritional value.
- The physical characteristics of an oil or fat are dependent on such factors as seed or plant source, degree of unsaturation, length of carbon chains, isomeric forms of the fatty acids, molecular structure of the glycerides, and processing.

So, we have earlier also discussed and you know by now that oil constitute one of the essential component of balanced diet as good source of energy. The chemical and physical properties of oil are among the most important properties that determine the quality and help to describe the present condition of oils. Physical, chemical and nutritional properties of vegetable oils vary significantly depending upon the type of fatty acid present in the oil. Vegetable oils also contain other compounds in minor amount as we have discussed already earlier and these minor components of the vegetable oil affect their quality and nutritional value. The physical characteristics of an oil or fat are dependent on the such factors or plant sources, degree of unsaturation, length of carbon chains, isomeric forms of fatty acid present in the triglyceride, molecular structure of the glyceride and the processing parameters. So, all these factors influence the physical characteristics of the oils and fats.

- During extraction, purification and usage, oils undergo a variety of processing operations, including frying, distillation and chemical modification which may alter their properties.
- The physical properties of edible oils depend primarily on composition (and hence on biological origin) and temperature.
- Prediction of the behavior of oils under real processing conditions from molecular properties is beyond current understanding.
- Semi-empirical equations are developed that relate the property of interest (e.g., time for fat to drain from a fried potato chip) to independently measurable bulk properties (e.g., density, viscosity, and surface tension).
- With these equations, it is possible to predict how changes in the properties of an oil alter the efficacy of a process.

During extraction, purification and usage, oils undergo a variety of processing operations including frying, distillation and chemical modifications which may also significantly influence their properties depending upon the process parameters are used like cooking temperature, frying temperature and so on. The physical properties of edible oils depend primarily on composition and on the biological origin as well as the temperature to which it is exposed to. Prediction of the behaviors of oil under real processing conditions from molecular properties is beyond current understanding. Semi empirical equations are developed that relate the property of interest like for example, time for fat to drain from the fried potato chips or such products to independently measurable bulk properties such as density, viscosity and surface tension. With these equations, it is possible to predict how the changes in the properties of an oil alter the efficiency of a process. There are several such equations in the literature and we will cite a few whenever it is necessary in this course we will take up.

Common physical properties of edible oil are

- Density
- Specific gravity
- Viscosity
- Optical
- Thermal
- Rheological
- Crystallization & polymorphism

- The density of a material is a measure of the mass per unit volume.
- The density of most food oils is less than that of water.
- In general, the density of an oil decreases with molecular weight and increases with unsaturation.
- Several researches have developed empirical functions to relate vegetable oil density to fatty acid composition and temperature.
- The density of oil decreases linearly with temperature.

So, now let us have a look of some of the properties and the common physical properties of edible oil which everyone as a processor, as a manufacturer, as a exporter, as a producer of the oil should be concerned with are the density, specific gravity, viscosity, optical property, thermal properties, rheological properties and finally, and most importantly from processing and food formulation point of view crystallization and polymorphism. The density of a material is a measure of the mass per unit volume. The density of most food oils is less than that of water. In general, the density of an oil decreases with the molecular weight and increases with the unsaturation of the fatty acids. Several researchers have developed empirical functions to relate vegetable oils to fatty acid composition and temperature. The density of oil decreases linearly with the temperature.
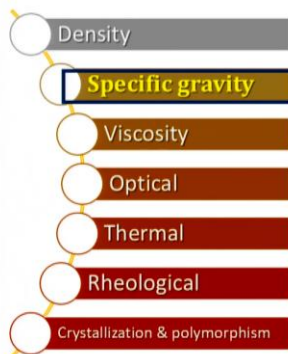
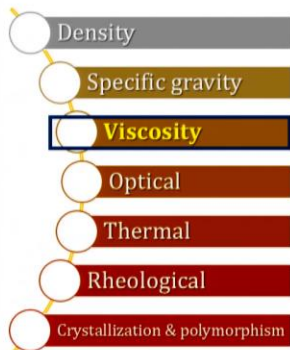Other property important property is specific gravity which is commonly used in conjunction with other figures in assessing the purity of the oil. This is a dimensionless unit defined as the ratio of the density of the substance to the density of water at a specified temperature. The specific gravity of vegetable oil is usually about 0.910 to 0.920 at 25°C. And in this figure, the specific gravity of some common vegetable oil like groundnut oil, mustard oil, soy oil, coconut oil, palm kernel oil, olive oil, sesame oil, palm oil and in the y axis is the specific gravity are shown. So, you can in this bar diagram, you can see groundnut oil has little more specific gravity or it is 0.92 and that next in the soybean oil it again about 0.925, same is about sesame oil and palm oil. The olive oil is less dense among all these oils as you can see in this bar diagram.

□ **Common physical properties of edible oil are**

- Density
- Specific gravity
- **Viscosity**
- Optical
- Thermal
- Rheological
- Crystallization & polymorphism

- **Viscosity** is a measure of intermolecular friction in a fluid and hence of its resistance to flow.
- Food oils behave as ideal Newtonian liquids over a wide range of shear rates and therefore may be characterized by a single viscosity.
- Viscosity of oils decreases exponentially with increasing temperature.
- The viscosity of water is much less (~2%) than that of most oils.

Then the next property becomes viscosity. It is a measure of the intermolecular friction in a fluid and hence of its resistance to flow. Viscosity is the property that which indicates a resistance to flow. Food oils we have as a ideal Newtonian liquids over a wide range of shear rate and therefore, may be characterized as by a single viscosity. Viscosity of oils decreases exponentially with increase that increasing the temperature. The viscosity of water is much less that is the 2% approximately than that of the most of the oils.

Comparison of bulk physical properties of edible oils with water

	Oil	Water
Molecular weight (g/mole)	885	18
Melting point (°C)	5	0
Density (kg m^{-3})	910	998
Compressibility (m s^2 kg^{-1})	5.03×10^{-10}	4.55×10^{-10}
Viscosity (mPa s)	≈50	1.002
Thermal conductivity (W m^{-1} K^{-1})	0.170	0.598
Specific heat capacity (J kg^{-1} K^{-1})	1980	4182
Thermal expansion coefficient (°C^{-1})	7.1×10^{-4}	2.1×10^{-4}
Dielectric constant	3	80.2
Surface tension (mN m^{-1})	≈35	72.8
Refractive index	1.46	1.333

Source : Fennema's Food Chemistry, 2007

A comparison of the physical properties of edible oil with that of the water is given in the table and you can see the molecular weight is of the oil is much higher than that of the water, ok. And melting point density, compressibility, viscosity, and other parameters are also provided here in the data. In this table you can see that thermal expansion coefficient of the oil is around 7.1×10^{-4}, whereas for water, it is 2.1×10^{-4}. Dielectric constant of oil is 3, whereas for the same per water is 80.2. Similarly surface tension, refractive index, etc is also provided there.

Then the other important property is the optical properties. These optical properties of lipids influence the overall appearance of many food material in which they are used. Certain optical properties of lipids can be used to provide valuable information about their composition or quality. The most important optical properties of lipids are their refractive index and their absorption spectra.

The refractive index is based on the ratio of the speed of a light wave in air as compared to its speed in the fat substance. The refractive index of a particular oil is mainly determined by the molecular structure of the fatty acid that it contains. The refractive index tends to increase with increasing chain length, increasing number of double bonds and increasing conjugation of double bonds. Empirical equations have been developed to relate the molecular structure of lipids to their refractive indexes. Measurements of refractive index of liquid oil can be used to provide some information about the average molecular weight or degree of unsaturation of the fatty acids that they contain.

Absorption spectra

- Measurements of the UV-visible absorption spectra of oils can also provide valuable information about their composition, quality, or molecular properties.

e.g. Conjugated dienes adsorb UV light around 232 nm, whereas conjugated trienes adsorb around 270 nm.
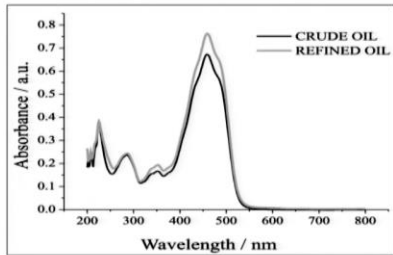
Absorption spectra of crude vs refined oil

- The absorption spectrum of an oil can also have a pronounced influence on the final appearance of a food product.

- Pure triacylglycerols have little inherent color because they do not contain groups that adsorb light in the visible region of the electromagnetic spectrum.

Source : Aquino et al. (2012)

The absorption spectra that is normally measurements of UV absorption spectra of oils can also provide a valuable information about their composition, quality or molecular properties. For example, conjugated dienes absorb UV light at around 232 nm whereas the conjugated trienes absorb UV light at around 270 nm. The absorption spectra of crude as well as refined oil can be seen in the figure here. X-axis is wavelength and nanometer and in the Y-axis it is shown the absorbance. The absorption spectra of an oil can also have a pronounced influence on the final appearance of a crude product. Pure dry glycerols have little inherent color because they do not contain groups that absorb light in the visible region of the electromagnetic spectrum.

The thermal properties, the most important thermal properties of lipids from a practical stand point of view in the food processing are specific heat capacity that is commonly known as C_P, thermal conductivity K, melting point T_{MP} and enthalpy of fusion that ΔH_F.

The specific heat capacity and thermal conductivity of some of the liquid oils, their physical properties at 20 °C are given in this table that is the water, sunflower, corn, olive and their value C, alpha, C_P, ρ, specific gravity, β, τ, etc all these things are like ultrasonic velocity,

attenuation, specific heat at constant temperature, C_P that is the density is ρ, absorption, adiabatic expansion coefficient B, viscosity η and thermal conductivity τ that is these values are given in the table. And you can see from this here that a specific heat capacity of the most liquid oils and solid fats are at around 2 joules per kg per Kelvin and it increases with increasing temperature. Lipids are relatively poor conductors of heat and tend to have appreciably lower thermal conductivity that is at around 0.170 watt per meter per degree Kelvin and the water that is the which has thermal conductivity of around 0.598 watt per meter per kg. So, these oil they have considerably lower thermal conductivity than the oil than the water.

Melting point and heat of fusion of a lipid depend upon the packing of the triacylglycerol molecules within the crystals formed that is the more effective the packing, the higher the melting point of the and the enthalpy of fusion. Melting points and heat of fusions of pure triacylglycerols tend to increase with the increasing chain length and they are higher for saturated fatty acids than for unsaturated fatty acids. Triacylglycerol which have more straight chain fatty acids their melting point and heat of fusion will be more in comparison to those which have symmetrical distribution of fatty acids. That is the triacylglycerols which has more trans fat they will have more melting point than those which have cis fats ok. These melting points are higher for more stable polymorphic form in comparison to those for the less stable polymorphic forms.

Factors that determine the melting behavior

- Average chain length of the fatty acids - In general, the longer the average chain length, the higher the melting point.

- Positioning of the fatty acids on the glycerol molecule also affects the melting point. As an example, safflower oil, which has a long average chain length, will melt like a medium chain length triglyceride.

- Relative proportion of saturated to unsaturated fatty acids - The higher the proportion of unsaturated fatty acids, the lower the melting point.

- Processing techniques such as the degree and selectivity of hydrogenation and winterization.

Triacylglycerol	Melting Point (°C)	ΔH_f (J g^{-1})
LLL	46	186
MMM	58	197
PPP	66	205
SSS	73	212
OOO	5	113
LiLiLi	−13	85
LnLnLn	−24	—
SOS	43	194
SOO	23	—

L = lauric acid (C12:0), M = myristic acid (C14:0), P = palmitic acid (C16:0), S = stearic acid (C16:0), O = oleic acid (C18:1), Li = linoleic (C18:2), Ln = linolenic (C18:3).

Source : Fennema's Food Chemistry (2007)

So, factor that determine the melting behaviour of a food oil or fat depends upon the average chain length of the fatty acids. In general the longer the average chain length as I told you earlier also higher will be the melting point. Then other factor is the positioning of the fatty acid on the glycerol molecule it also affects the melting point. As an example, safe flour oil which has a long average chain length will melt like a medium chain length triacylglycerol. Relative proportion of saturated to unsaturated fatty acids is another factor. The higher the proportion of unsaturated fatty acids the lower will be the melting point. Processing techniques such as the degree and selectivity of hydrogenation and winterization are also important factors that influence the melting behaviour of fats and oil.

Then thermal stability of lipids it is another important parameter and which is very helpful in deciding the usefulness as well as stability of the food oils and fat in the processing operations. Its usefulness in the food processing and for selecting the oils and fat for a specific operation. So, the important properties which determine the thermal stability include smoke point which is the temperature at which the sample begins to smoke when tested under specified conditions. Flash and fire point are other properties the flash point is the temperature at which the volatile products generated by the lipid are being produced at a rate where they can be temporarily ignited by application of a flame, but they cannot sustain combustion. The fire point is the temperature at which the evolution of volatiles because of the thermal decomposition occurs so quickly that continuous combustion can be sustained after application on a flame.

Smoke point of certain some of the common oils is given in this diagram. There is a like avocado it is smoke point is 550° whereas, rice bran oil has 470°, palm oil 466, even corn oil 450°, canola 400, virgin and extra virgin olive oil 380°, etc. So, common that is a vegetable oils they are this smoke point and all these points are given in the degree Fahrenheit. So, measurements of these temperatures obviously, are particularly important ok. When the selecting lipids that are going to be used at high temperature during baking, during frying etc. For example, if you want to fry a food at 300 degree Celsius let us say potato chips or any other product ok and you want to select the which will be the useful oil for this then obviously, you there is no point of taking a oil which has a smoke point less than 300 degree Celsius.

So, you have otherwise you have to have the oil which has smoke point at least somewhat greater than the 300 degree Celsius. So, that you can heat that oil that is here smoke point is the one which is a maximum temperature up to which the oil can be heated above that point it will just catch fire. The thermal stability of triacylglycerol is much better than that of the free fatty acids. Thus the property of lipids to break down during heating is largely determined by the amount of volatile organic material that they contain such as free fatty acids etc.
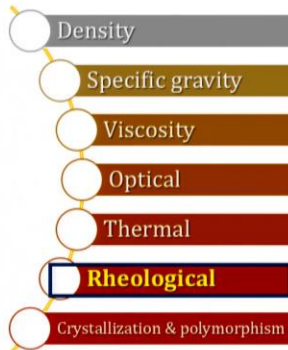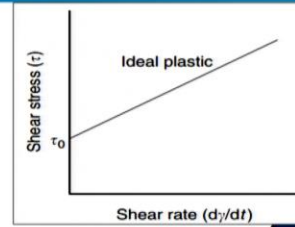
The other important physical properties of the oil include rheological properties. Most liquid oils are Newtonian liquids with intermediate viscosity typically between 30 and 60 milli Pascal second at room temperature. Most solid fats actually consist of a mixture of fat crystals dispersed in a liquid of matrix. The rheological properties of these solid fats are highly dependent on the concentration, morphology, interaction and organization of the fat crystals that are present in the system.

Source : Fennema's Food Chemistry (2007)

Plasticity is another important characteristics it is a important rheological characteristic like solid fats exhibit a type of rheological behavior and it is known as plasticity. And a plastic material behaves like a solid below a critical applied stress known as yield stress, but it behaves a liquid above this stress and you can see here that is the relationship that is for Bingham plastic fluid that is relationship between shear stress and shear rate that is given. So, it will indicate that at which stress it will behave like a solid and where it will behave like a liquid. The rheological behavior of an ideal plastic material known as Bingham plastic is shown in this figure. For an applied shear stress the rheological characterization of this type of material can be described by the equation
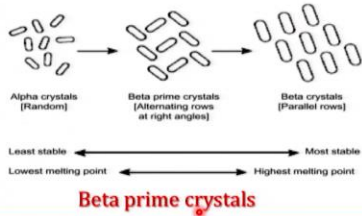
$$\tau = G\gamma \ (for \ \tau < \tau_0)$$

$$\tau - \tau_0 = \eta\dot{\gamma} \ (for \ \tau \geq \tau_0)$$

where τ is the applied shear stress, y is the resultant shear strain, $\gamma^.$ is the rate of shear strain, G is the shear modulus, η is the shear viscosity and τ_0 is the yield stress that is the point where the material starts to flow. So, this property here using this you can calculate the rheological the rheological characteristics of the Bingham plastic foods.

Plasticity (Contd...)

- At 70°F (21°C), a typical shortening that appears solid contains 15-20% solids & hence, 80-85% liquid oil.
- Through proper selection of oil/oils, processing techniques, and control, this small amount of solids can be made to hold all of the liquid in a matrix of a very small, stable, needlelike crystals (beta-prime crystals).
- Below a certain applied stress there is a small deformation of the sample, but the weak bonds between the fat crystals are not disrupted.

Alpha crystals [Random] → Beta prime crystals [Alternating rows at right angles] → Beta crystals [Parallel rows]

Least stable ← → Most stable
Lowest melting point ← → Highest melting point

Beta prime crystals

- When the critical yield stress is exceeded, the weak bonds are broken and the fat crystals slide past one another leading to flow of the sample.
- Once the force is removed the flow stops, and the fat crystals begin to form bonds with their neighbors again.

Perera & Perera, 2019

At 70 degree Fahrenheit or 21 degree Celsius a typical shortening that appears solid contain around 50 to 20 percent solid and hence 80 to 85 percent liquid oil you see, but it looks like solid. Through proper selection of oil or oils processing techniques and control this amount of small amount of solids can be made to hold all of the liquids in a matrix of a very small stable needle like crystal which is generally known as beta prime crystals you can see here. Below a certain applied stress there is a small deformation of the sample, but there is weak bonds between the fat crystals are not disrupted ok. When the critical yield stress is exceeded the weak bonds are broken and the fat crystals slide past one another leading to the flow of the sample and once the force is removed the flow stops and the fat crystals begin to form bonds with their neighbors again. So, here you see that is the three types of crystals which can form the fats depending upon the different triglycerides and other conditions present at the end. That is the alpha crystals which are random, beta crystals which are like parallel rows and beta prime crystals where you can see here alternating rows of right angles. That is the beta crystals are most stable whereas, the alpha crystals are least stable beta prime in this middle in between they have the stability that is average of alpha and beta. Similarly that the beta crystals have highest melting point and alpha crystals have lowest melting point and this beta prime crystals obviously, they have the intermediate melting point.

Solubility

- The solubility of vegetable oils in aqueous ethanol depends on the concentration of alcohol and temperature of the system.
- At ordinary temperatures even absolute alcohol is not a good solvent for vegetable oils since the solubility is even less than 10 g of oil per 100 g of alcohol.
- With increasing temperatures, the rapidity and completeness of solubility increases.
- Mowrah, safflower, peanut, and cottonseed oils are soluble in absolute alcohol at 70°C.
- All the oils investigated are found to be miscible above the boiling point of alcohol even if the concentration is 98%.
- In 95% ethanol they are miscible between 90° and 100°C.
- Addition of a good solvent, like n-hexane, increases the solubility of oils, and the solubility temperatures are lowered.

The solubility of vegetable oils in aqueous ethanol depends upon the concentration of alcohol and temperature of the system. Solubility is very important properties of the triglycerides. At ordinary temperature even absolute alcohol is not a good solvent for vegetable oil since the solubility is less than 10 gram of oil per 100 gram of alcohol. With increase in temperature the rapidity and completeness of the solubility increases. Mowrah, safflower, peanut and cottonseed oils are soluble in absolute alcohol at 70 degree Celsius. As the oils investigated are found to be miscible above the boiling point of the alcohol even if the concentration is 98 percent all the oils are found to be miscible. In 95 percent ethanol they are miscible between 90 degree and 100 degree Celsius. Addition of a good solvent like n-hexane increases the solubility of oil and the solubility temperatures are lowered.
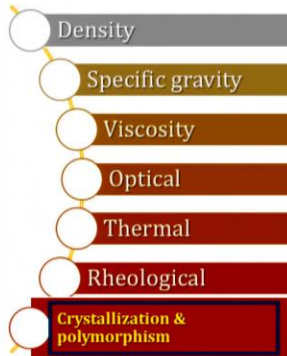
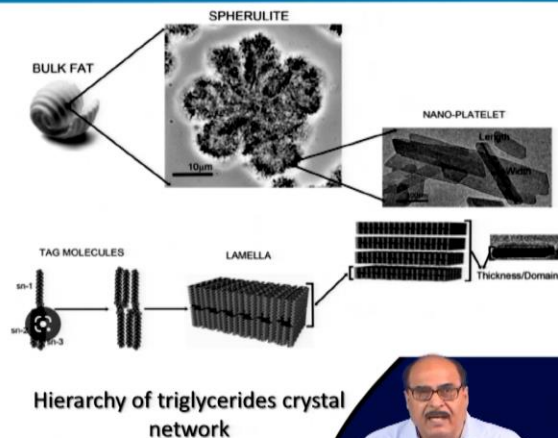The other important property is the crystallization and polymerization. The physical state that the solid or liquid of the lipids in many food products plays an important role in their production and in determining their final quality attributes. The creation of food products with desirable properties therefore, depends upon an understanding of the major factors that influence the crystallization and melting of lipids in foods.

Hierarchy of triglycerides crystal network

Source : Marangoni et al., 2012

And one is the important contribution is the contribution is of the solid fat content that is important parameter. The physical state of the lipid in a food is usually characterized in the form of the solid fat content which is the presence percentage may be 0 to 100 percent of the lipid that is solid at a particular temperature. The solid fat content falls from 100 to 0 percent when the temperature is increased from below to above the melting point. As mentioned earlier the desirable plastic rheological properties of edible fats usually occur over the range of temperatures where the lipids are partially crystalline. A bulk fat consists micro structurally of spherulites as you can see here in the figure, which in turn composed of crystalline nanoplatelets assembled from crystalline lamellae of the triglycerides that is a nano lamellae finally, give that the crystalline extra bulk fat spherulite ok. It is spherulites you can see here in the figure and how these are formed that is the from the triacylglycerol molecule, then lamellae, then nano platelets and finally, the spherulites structure.

Crystallization (Contd...)

- A liquid-to-solid transition (crystallization) is exothermic because energy is released as the molecules come closer together.

❖ **Supercooling**

- The degree of supercooling of a liquid can be defined as

$$\Delta T = T - T_{mp}$$

Where, T is the temperature

T_{mp} is the melting point

- The value of ΔT at which crystallization is first observed depends on the chemical structure of the lipid, the presence of any contaminating materials, the cooling rate, the microstructure of the lipid phase (e.g., bulk vs. emulsified oil), and the application of external forces.

A liquid to solid transition that is the crystalline is exothermic because energy is released as the molecule come closer to each other. And there are three stages that is the one is the super cooling the degree of super cooling of a liquid can be defined as

$$\Delta T = T - T_{mp}$$

where T is the temperature and T_{mp} is the melting point. And the value of ΔT at which crystallization is first observed depends upon the chemical structure of the lipid, the presence of any contaminating material, the cooling rate, the microstructure of the lipid phase like bulk versus emulsified oil and the application of external forces etc. So, there is the for crystallization first the cooling occurs and then comes the nucleation

When the materials is cooled down, then the nucleus starts first nucleus is small nucleus is formed and which enlarges into the form of crystal. So, crystal growth can only occur after the stable nuclei have been formed in a lipid. These nuclei are believed to be cluster of oil molecules that form small ordered crystallites that are created when a number of lipid molecules collide and become associated with each other. There is a free energy change associated with the formation of one of these nuclei. The total free energy change associated with the formation of a nuclei is therefore, a combination of a volume and a surface term and that can be found out using these equations that

$$\Delta G = \Delta G_V + \Delta G_S$$

$$\Delta G = \frac{4}{3}\pi r^3 \frac{\Delta H_{fus}\Delta T}{T_{mp}} + 4\pi r^2 \gamma_i$$

r is the radius of the nuclei delta H_{fus} is the enthalpy change per unit volume associated with the liquid solid transition which is negative normally and γ_i is the solid liquid interfacial tension. So, using this equation one can find out.

Then the rate at which nucleation occurs can be mathematically related to the activation energy that is delta G that must be overcome before stable nuclei are formed that is

$$J = Aexp\left(-\frac{\Delta G^*}{kT}\right)$$

where J is the nucleation rate which is equal to the number of stable nuclei per second per unit volume of material. A is the pre exponential factor, k is Boltzmann constant and T is the absolute temperature.

Then there might be two types of nucleation one is the homogeneous nucleation other may be heterogeneous nucleation that is homogeneous nucleation occurs when no impurities are present in the oil. The formation of stable nuclei negligibly slow at slow at temperature just below the melting point, but increases dramatically when the liquid is cooled below a certain temperature like that ok. Heterogeneous nucleation occurs when liquid oil is in contact with foreign substances such as surfaces of dust particles, fat crystals, oil droplets or air bubbles, reverse micelles or vessel containing the oils. Then nucleation can be induced at higher temperature that expected from a pure system. Then once nucleation is then these nuclei once nuclei are formed they try to enlarge that is called crystal growth. They grow into crystals by incorporating molecules from the liquid oil at the solid liquid interface.
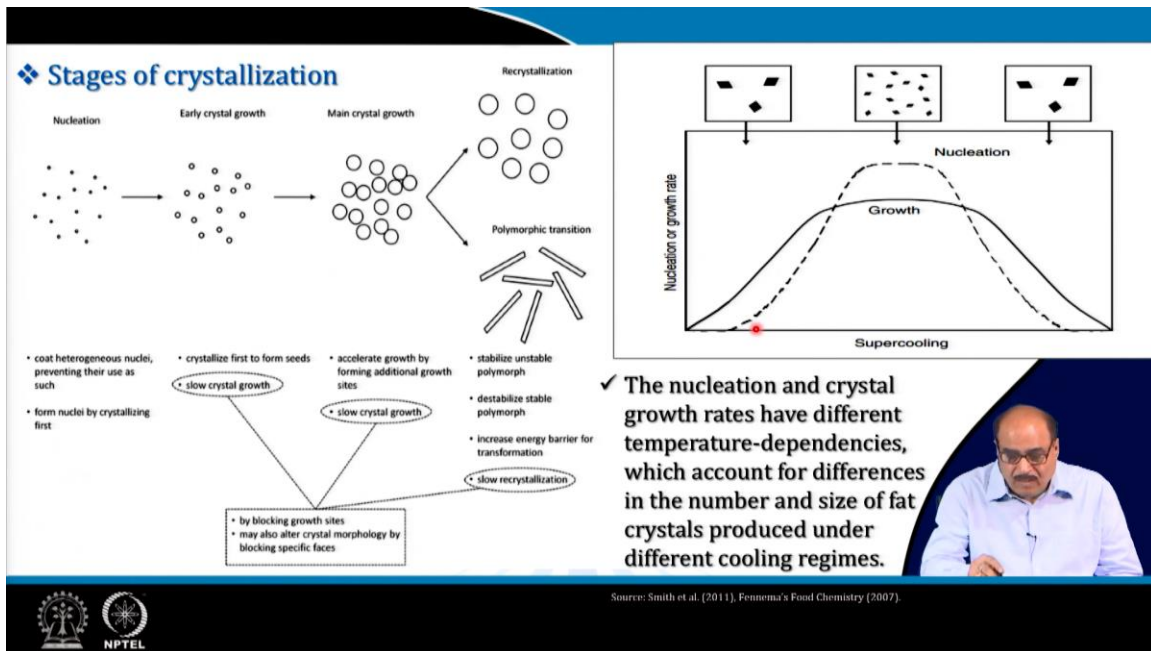
And here in this figure you can see the stage of crystallization that nucleation and crystal growth rates have different temperature dependencies which account for differences in the number and size of the fat crystals produced under different cooling condition. And you can see here that the this figure that is the super cooling that the rate in the nucleation of growth nucleation of the growth rate how it is influenced by this rate of the nucleation and this is the rest of the crystal growth. And I told you that it depends upon the temperature have different temperature dependency. And accordingly different types of crystals are formed that is nucleation, then early crystal growth, then main crystal growth and finally, you get recrystallization and polymer polymorphic transition. That is in the nucleation there is the it coat heterogeneous nuclei preventing their use such as from the nuclei variety crystallizing fat ok. And the crystal growth will be slow crystal growth in the earlier stages and there will be by blocking the growth side, it may also alter crystal morphology by blocking the specific fat etc. And once that is in the final stage during processing that is unstable polymorphs are there they destabilize stable polymer or increase the energy barrier for the transition etc ok.

So, you can see here that is the post crystallization what happens that is the structure during processing how they are formed and then finally, in the storage what happens that is the post crystallization involves a change from a less stable to a more stable polymorphic form because of the rearrangement of the triacylglycerol molecules the post crystallization process. If a lipid forms mixed crystals, then there may be a change in the composition of the crystals during storage because of the diffusion of triacylglycerol molecules between the crystals. There may also be net growth in the average size of the crystals within a lipid with the time to Oswald ripening. Finally the bonds between fat crystals may straighten over the time during storage owing to a there is sintering mechanism that is fusion of the crystal growth together and that is called recrystallization. So, that crystallization crystal growth 0 to 10 minutes, then aggregation gel formation network compaction and then finally, recrystallization during storage. So, these are the stages and that finally, what the gives that polymorph that is the accordingly the conditions should be formed that is heat of fusion or even heat of crystallization removal etc. This should be it also be tempered properly to have a proper molecular surface and beta prime crystals are better considered for various purposes.

❑ **Polymorphism**

• Triacylglycerols exhibit a phenomenon known as (monotropic) polymorphism, which is the ability of a material to exist in a number of crystalline structures with different molecular packing

• The three most commonly occurring types of packing in triacylglycerols are hexagonal, orthorhombic, and triclinic, which are usually designated as α, β' and β polymorphic forms, respectively

• The thermodynamic stability, and thus the melting point, of the three forms decreases in the order: β>β' > α.

• Triacylglycerols often crystallize in the α form initially because it has the lowest activation energy for nuclei formation

• With time the crystals transform to the most stable polymorphic form (β) depending on temperature, pressure, and the presence of impurities
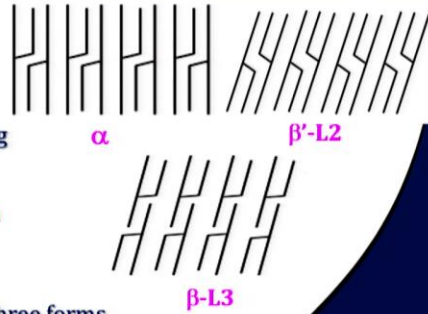
So, the polymorphism that is here is triacylglycerols exhibit a phenomenon known as monotrophic polymorphism which is the ability of a material to exist in a number of crystalline structures with different molecular packing. You can see that alpha, beta, beta prime L2 and beta L3. The three most commonly occurring types of packing in triacylglycerol are hexagonal, orthorhombic and triclinic that is the usually that is hexagonal is alpha is alpha gonal and this alpha, beta prime and beta polymer. So, alpha is hexagonal, beta prime is the orthorhombic and beta is the triclinic. The thermodynamic stability and thus the melting point of these forms decrease in the order that is the beta, beta' and that is the beta is more had more melting point more stable than the beta' than the alpha.

Triacylglycerols often crystallize in the alpha form initially because it has the lowest activation energy for nuclei formation with time crystal transformation to most stable polymorphic form that is beta depending upon the temperature, pressure, and the presence of impurities.

So, the knowledge of polymorphic form from the crystals in the lipid is often important because it can have a large impact on the thermal behaviour and morphology of the ice crystal form and therefore, on the physicochemical and sensory properties of the foods. Finer beta crystals are preferred in the margarine and spreads where smoothness, gloss and a high degree of surface coverage of disperse water is required. Larger beta mono polymorphic forms are often preferred in a bakery shortening for example, lard to create flakiness and cocoa butter stability in chocolate. So, blending of the lipids may also be used to control whether the beta or beta prime polymorphs are the predominate crystal habits which are formed.

Polymorphic form of fat crystals

Source : Marangoni (2004)

So, here the various polymeric form finally, is shown here that is a transition pathways showing that these are the dotted arrow thin arrows are exothermic reactions and thick arrows are endothermic reactions. You can see that how this liquid oil it transform into the various form alpha form, beta' form and beta form that what we discussed earlier. The same is a in pictorially presented in this case.

Summary

- Physical, chemical and nutritional properties of oils vary depending on the type of fatty acids present in the oil.
- Physical and chemical properties of the oil depends on the fatty acid composition.
- The bulk properties of the oil are density, viscosity, melting point, specific heat capacity, thermal conductivity, etc.
- Fat undergoes crystallization process through super-cooling, nucleation, and crystal growth.
- Triacylglycerols exhibit polymorphism, which is the ability of a material to exist in a number of crystalline structures with different molecular packing.

So, finally, I would like to summarize this lecture that here the physical, chemical and nutritional properties of the oils play a very important role and they vary depending upon the type of fatty acid present in the oil. Physical and chemical properties of the oil depends upon the fatty acid composition, the bulk properties of the oils are density, viscosity, melting point, specific heat capacity, thermal conductivity etc. Fat undergoes crystallization process through super cooling, nucleation and crystal growth and triacylglycerol exhibit polymorphism which is the ability of a material to exist in number of crystalline structure with different molecular packing and this polymorphs that is they decide they are helpful in using these fats in the various bakery operation, various other product manufacturing etc. So, this is the references which has been used in this lecture.

References

- Aquino, J. D. S., Pessoa, D. C., Araújo, K. D. L. G., Epaminondas, P. S., Schuler, A. R. P., Souza, A. G. D., & Stamford, T. L. M. (2012). Refining of buriti oil (Mauritia flexuosa) originated from the Brazilian Cerrado: physicochemical, thermal-oxidative and nutritional implications. *Journal of the Brazilian Chemical Society, 23*, 212-219.
- *Cooking Oil Comparisons - Grate Bites.* (2018, March 29). Grate Bites. http://gratebites.com/cooking-oil-comparisons/
- Coupland, J. N., & McClements, D. J. (1997). Physical properties of liquid edible oils. *Journal of the American Oil Chemists' Society, 74*, 1559-1564.
- Damodaran, S., Parkin, K. L., & Fennema, O. R. (Eds.). (2007). *Fennema's food chemistry.* CRC press.
- Dunford, N. T. (2016). *Edible oil quality.* Oklahoma Cooperative Extension Service.
- *Food Science Corner: Fat Crystallization – An exclusive community for the food & beverage industry | FoodGrads.* (n.d.). https://foodgrads.com/food-science-corner-fat-crystallization/
- Ichu, Chigozie & Nwakanma, Henry. (2019). Comparative Study of the Physicochemical Characterization and Quality of Edible Vegetable Oils. International Journal of Research in Informative Science Application & Techniques (IJRISAT). 3. 10.46828/ijrisat.v3i2.56.
- Kaparthi, R., & Chari, K. S. (1959). Solubilities of vegetable oils in aqueous ethanol and ethanol-hexane mixtures. Journal of the American Oil Chemists' Society, 36(2), 77-80.
- Kumar, Ratnesh & Chandra, Suresh & Kumar, Kapil & Kumar, Vikrant & Kumar, Tarun & Samsher, and. (2018). Analysis of the physical and chemical characteristics of edible vegetable blended oil.

These are the references ok.

With this, thank you very much for your patience here. Thank you.