EFFECT OF COOLING RATE AND AGITATION ON FAT CRYSTALLIZATION: A MINI-REVIEW

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Abstract. Fat is a material that is widely utilized as a raw material in various industries including pharmaceutical, cosmetic, and food industries. One of the concerns is the ability of fat to form crystals. Cooling and agitation rates play an important role in fat crystallization. Variables such as temperature, composition and molecular structure affect the dynamic process by which fats solidify and form crystals during cooling. Although many studies have been conducted on fat crystallization, the effects of agitation and cooling rate on the crystal structure and properties of fats still require further re-search. This article aims to review the current knowledge on fat crystallization, emphasize shortcomings in current research, and present experimental results that illuminate the role of cooling rate and agitation in the formation of characteristic fat crystals

Keywords: agitation rates, crystalline fat, fat crystallization, lipid,

1 Introduction

Fat is a material that is widely utilized as a raw material in various industries including pharmaceutical, cosmetic, and food industries. Its function can be a carrier matrix for certain target compounds or even as a product coating [1]. One of the concerns is the ability of fat to form crystals. In fat crystallization, there are several factors that must be considered, including the mechanical properties of fat (texture, firmness, spreadability, physical stability of fat, sensory characteristics (mouthfeel and meltability) and visual appearance of the product.

Cooling and agitation rates play an important role in fat crystallization. Variables such as temperature, composition and molecular structure affect the dynamic process by which fats solidify and form crystals during cooling. Although many studies have

been conducted on fat crystallization, the effects of agitation and cooling rate on the crystal structure and properties of fats still require further research.

This article aims to review the current knowledge on fat crystallization, emphasize shortcomings in current research, and present experimental results that illuminate the role of cooling rate and agitation in the formation of characteristic fat crystals.

2   Fat crystallization mechanism

Crystalline fats can aggregate to form a 3-dimensional (3D) network in an oil phase. The mechanical properties of this 3D network depend on the chemical composition and process conditions [2]. According to Marangoni and Wesdorp [3], the formation of crystalline fat networks usually occurs in several stages including (a) formation of stable nuclei (b) incorporation into lamellar forms, (c) incorporation of fat to form nano-platelet crystals (CNPs) (d) aggregation of CNPs (e) formation of combined CNPs (f) random arrangement of combined CNPs to form crystallites (g) aggregation of crystallites to form crystals (h) formation of 3D networks. This mechanism can be seen in Fig. 1.
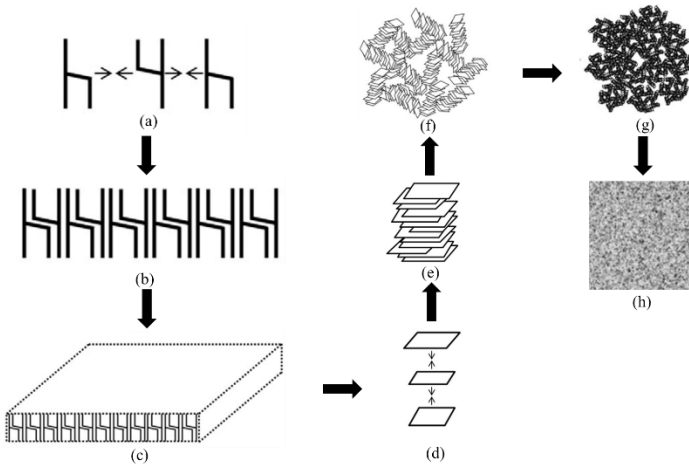
Fig. 1. Mechanism of fat crystal network formation.

Fat crystallization occurs through the process of nucleation and crystal growth. When the fat melt is cooled to a temperature below the melting point of the highest melting point of TAG (undercooling), it will cause the fat to be in the super saturated phase and lead to nucleation. TAG will experience constant fluctuation and movement as a result of heat energy and brown motion which causes a dynamic association and dissociation process. Nucleation can be divided into two categories, namely primary and secondary. Primary nucleation occurs through spontaneous formation of homogeneous or heterogeneous nuclei where the presence of minor components such as

emulsifiers or contaminants act as foreign nucleating agents that can trigger nucleation. Secondary nucleation is a nucleation process that arises due to the presence of preformed crystals in the system.

The nature of TAG (mono or mixed free fatty acids, chain link length, degree of saturation) and process conditions (cooling rate, agitation/shear, and process temperature) will affect how TAG will form crystals. The result of fat crystallization (TAG) will produce polymorphs that aim to improve molecular organization, density, stability, and crystal size. Three types of polymorphs produced by fat crystals include α, β', and β. In the α form, the subcell has a hexagonal shape where the TAG molecule is surrounded by 6 molecules that can rotate around its axis. The β' polymorph forms an orthorhombic (O$\perp$) subcell, where TAGs form perpendicular lines to each other. While in polymorph β forms a triclinic subcell (T//), where TAGs form a parallel composition. The nature of TAG fatty acids will affect the structure of their bond chain length. For example, two long-chain fatty acids will usually form when there are three fatty acids in the same or similar TAG. Triple chain length (3L) is formed when one fatty acid in the TAG is very different compared to the other fatty acids, for example, one fatty acid is shorter than the other fatty acids or contains a cis-unsaturated bond. TAG chain length organization plays an important role in combining properties between different TAGs and can be characterized using small-angle X-ray diffraction (SAX) [1, 4].

Crystallization of TAG mixtures will usually trigger the formation of crystals that incorporate more than one type of TAG known as crystalline compounds. The crystalline compound can form a solid, however, it does not have to be homogeneous. There are some crystalline compounds that consist of different TAG compositions. During crystallization, crystalline compounds more easily form α-crystals because they have a higher arrangement of free molecular degrees. Crystalline compounds can also form β' crystals, but this cannot happen immediately due to higher density values and movement restrictions.

3   Effect of agitation process on fat crystallization

The formation of fat crystal networks can be influenced by agitation (shear), the mixing process through the impeller and geometry conditions on the rheometer. Understanding the effect of agitation on the nucleation and crystallization process is related to industrial applications, where materials are subjected to agitation or mixing during the process to increase mass and heat transfer, improve product homogeneity, and improve process optimization.

The agitation process can increase the primary nucleation rate by providing sufficient energy to meet the energy limitation required to initiate nucleation. Increased nucleation results in more small crystals that can further transform into a network of fat crystals with higher mechanical strength. This depends on the aggregation properties of the fat crystal components. The agitation process can also accelerate the crystallization rate resulting in higher initial SFC values, but over time the SFC values will equilibrate. In addition, the agitation process can enhance secondary nucleation by destroying new crystal formation and distributing it, leading to increased nucleation seedlings

and crystal growth. The effect depends on the agitation rate (shear) where when conditions are above the critical rate, it will result in a smaller average crystal size as a result of breaking large crystals or inhibiting crystal growth and aggregation [5-6]. When under critical agitation rate conditions, it will produce larger crystals as a result of increased collision frequency and contact time between crystallites [7].

Agitation can accelerate the phase transition into a stable polymorph form [8]. Agitation will destroy van Der Waals forces on weak polymorphs, allowing restructuring to form higher polymorphs. The acceleration of the polymorph transition can cause the formation of nanoplatelets during nucleation which can then become a template for higher polymorphs [6]. Mazzanti *et al.* [9] stated that agitation can induce the crystallite orientation of various types of fat (cocoa butter, milk fat, palm oil). Comparing the crystalline milk fat with stripped milk fat (without polar minor fat), it was shown that polar minor fat acts as an impurity, which blocks crystallization, stabilizes α-crystals, and inhibits polymorph transformation to the more stable β′ form.

Tran *et al.* [10] characterized and described the mechanism of spheroidal crystal formation using a fat model system consisting of Fully hydrogenated canola oil (FHCO) and canola oil (CO), and using laminar shear with parallel plates in rheometer geometry. The results show that the formation of crystal balls is influenced by the cooling rate, obtaining an optimum/critical value of 1.0°C/min. When the cooling rate value is higher, it will inhibit the crystallization process because fat crystallization takes place quickly which causes a lack of time to induce crystals, and when the cooling rate value is lower, it affects the formation of crystals to a higher polymorph. A higher agitation rate decreases the crystal ball size and viscosity of the sample. This shows that crystal size and morphology will affect the rheological characteristics of the sample. The highest agitation rate will cause exhaustion and polymorph transition resulting in a smoother surface and decreased area. A decrease in area will result in a decrease in contact time and friction between particles resulting in lower viscosity. Nanoplatelet crystals (CNP) are initially thought to be cylindrical. Furthermore, the cylindrical CNP will undergo rotation and change its position to parallel. In this position, it can allow merging between cylindrical CNPs by damaging the weakest point on the cylindrical CNP. The combined CNP will roll over and experience epitaxial growth. Different things happen when treated with a high agitation rate. This causes CNP aggregation to form cylindrical clusters.

4   Effect of cooling rate on fat crystallization

Another process that affects fat crystallization is the cooling rate. The faster the cooling rate will produce α crystals while the lower the cooling rate will produce polymorphs β′, and β. A faster cooling rate will result in higher initial solid fat content (SFC) values and the formation of more and smaller crystallites while a slow cooling rate will result in lower SFC values and fewer large crystals [11].

Wiking *et al.* [12] conducted research on the effect of different cooling rates on the crystallization of milk fat. The anhydrous milk fat was cooled from 65°C to 20°C with two cooling rates, namely 0.1°C/min and 10°C/min. The results of analysis using

Confocal laser scanning microscopy (CLSM) showed that crystals had formed when the temperature reached 20°C in the fast cooling rate treatment. Different cooling rates will produce different sizes and morphologies of fat crystals. The slow cooling rate produces larger crystals compared to crystals produced by the fast cooling rate. The crystal network at the fast cooling rate is more uniform and has a higher number of bridges between crystals.

Fat crystals obtained from fast cooling have an area below 250 μm^2 while the area of crystals from slow cooling is in the range of 50 μm^2 to more than 950 μm^2. In slow cooling, nucleation occurs at higher temperatures which results in the formation of fewer high purity nuclei. These nuclei can grow into larger crystals. The same thing was conveyed by Herrera and Hartel [2] who conducted research on the effect of cooling rate on the microstructure of milk fat mixtures. The results obtained showed that rapid cooling (5.5 °C/min) from 25-30 °C formed crystals with a smaller and more uniform size than slow cooling (0.2 °C/min).

DSC analysis of the crystallization profile shows that slow cooling causes crystallization to begin before the temperature reaches 20°C. While rapid cooling resulted in two-stage crystallization, the first crystallization occurred at 2.0 ± 0.1 min and the second crystallization occurred at 18.5 ± 0.6 min. Two-stage crystallization can be the result of transition from different polymorph forms, crystallization at different TAG fractions, or a combination of both [13.

The cooling rate also affects the solid fat content (SFC) of the fat. According to Martini *et al.* [14], the cooling rate affected the final SFC value in blends of high melting point milk fat fractions with sunflower oil. In contrast, according to Herrera and Hartel [2], the cooling rate showed no effect on the final SFC value of high and low melting point milk fat fraction blends. Meanwhile, Wiking *et al.* [12] stated that the SFC value of non-fractionized milk fat after 80 minutes was not affected by the cooling rate. From some of the literature, it shows that there is inconsistency regarding the effect of cooling rate on SFC value.

5   Conclusion

Fat crystallization can be influenced by cooling rate and agitation (shear rate) factors. The agitation process will accelerate nucleation and increase the number of small crystals, resulting in an increase in the strength of the fat crystal network. Agitation can also accelerate the polymorphic transition and impact nanoscale crystallization. This leads to a decrease in nanoplatelet crystal size at fast agitation rates. In addition, agitation can be used to form spheroidal (spherical) crystal microstructures.

The cooling rate will affect the formation of fat crystals. A fast cooling rate will produce a smaller and uniform crystal size. While the slow cooling rate will produce fat crystals that are large and non-uniform. Therefore, knowledge of the factors affecting fat crystallization is very important for industrial applications.

References

1. Sato K. Crystallization behavior of fats and lipids — A review. *Chemical Engineering Science*. 56: 2255–2265. (2001)
2. Herrera ML dan Hartel RW. Effect of processing conditions on crystallization kinetics of a milk fat model system. *Journal of the American Oil Chemists' Society*. 77(11): 1177–1188. (2000)
3. Marangoni AG dan Wesdorp LH. Structure and properties of fat crystal networks. Boca Raton (USA): CRC Press Taylor & Francis Group. (2013)
4. Walstra P. Physical chemistry of foods. New York (USA): CRC Press Taylor & Francis Group. (2003)
5. Kloek W , van Vliet T, dan Walstra P.Mechanical properties of fat dispersions prepared in a mechanical crystallizer. Journal of Texture Studies. 36: 544–568. (2005)
6. Maleky F. Smith A K, dan Marangoni A. Laminar shear effects on the crystalline alignments and nanostructure of a triacylglycerol crystal network. Crystal Growth & Design. 11: 2335–2345. (2011)
7. Tarabukina E, Jego F, Haudin J M, Navard P, dam Peuvrel-Disdier E. Effect of shear on the rheology and crystallization of palm oil. Journal of Food Science. 74(8):616–626. (2009)
8. Dhonsi D dan Stapley AGF. The effect of shear rate, temperature, sugar and emulsifier on the tempering of cocoa butter. Journal of Food Engineering. 77(4):936–942. (2006)
9. Mazzanti G, Guthrie SE, Sirota, EB, Marangoni AG, dam Idziak SHJ. Orientation and phase transitions of fat crystals under shear. Crystal Growth & Design. 3(5):721–725. (2003)
10. Tran T, Ghosh S, dan Rousseau. Spheroidal fat crystalmicrostructures formed with confined gap shearing. Crystal Growth & Design. 14,: 6383–6390. (2014)
11. Acevedo NC and Marangoni AG. Toward nanoscale engineering of triacylglycerol crystal networks. Crystal Growth and Design, 10(8), 3334–3339. (2010)
12. Wiking L, De Graef V, Rasmussen M, dan Dewettinck K. Relations between crystallisation mechanism and microstructure of milk fat. International dairy journal. 19:424-430. (2009)
13. Foubert I, Dewettinck K, Janssen G, Vanrolleghem PA. Modelling twostep isothermal fat crystallisation. Journal of Food Engineering. 75: 551–559. (2006)
14. Martini S, Herrera ML, dan Hartel RW. Effect of cooling rate on crystallization behaviour of milk fat fraction/sunflower oil blends. Journal of the American Oil Chemists Society. 79: 1055–1062. (2002)