Lipid crystallization kinetics - Roles of external factors influencing functionality of end products

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Abstract

The extent of crystallization and transformation of lipids, and their network formation, play decisive roles in determining physical properties (e.g., hardness, texture, rheology, and spreadability) of lipid-based food products. In these products, the lipid materials are present in rather complicated physical states such as mixtures of solid and liquid lipids or emulsified with water phases. In addition, various external influences are applied during actual production in a factory. Therefore, exploration of lipid crystallization under multiple external influences is necessary to improve the functionality of lipid-based food products.

Introduction

Lipids are major nutrients widely employed as lipophilic materials in confections, butter/spreads, ice creams, etc. Controlling physical properties of lipids has become increasingly significant both from the fundamental and applied points of view. Physical, chemical, biochemical, and biotechnological approaches have been developed to cope with current diversified market demands in the lipids industry, e. g., replacing *trans*-fatty acids with alternatives, reducing saturated fatty acids, and improving functionality of end products under processing, storage, and consumption conditions.

Major physical properties of lipid-based food products are gloss, hardness/softness, melting, texture, rheology, and spreadability. These physical properties are primarily influenced by three main factors: crystallization and transformation behavior, microstructures of lipid crystals, and rheological and textural properties exhibited by lipid crystal networks. Crystallization and transformation of lipids constitute an important body in the research of the physical properties of food lipids, which are mostly represented by triacylglycerols (TAGs) called fats. Lipids exhibit highly complicated crystallization behavior, and their physico-chemical properties (e.g., melting, rheology, morphology, and texture) are mainly determined by their fatty acid structures and compositions, which are most typically revealed in polymorphism. In addition, all lipid-based foodstuffs are made of aggregated poly-crystalline lipid crystals, whose networks are formed by crystallization conditions to reveal optimal size, shape, and orientation of lipid crystals having nanometer and millimeter dimensions. Otherwise, deterioration of the food products occurs in fat bloom in confections, draining of liquid oil from spreads, and water-oil separation in emulsion systems.

Thus, controlling the physical properties of lipids becomes an important challenge for industrial fields to obtain the desired product characteristics (**Figure 1**). Many studies have focused on determining molecular and crystalline structures, the influence of external factors on the crystallization and transformation mechanisms, the formation of lipid-crystal networks from nano-scale to meso- and macro-scale structures and rheological and textural properties. Extensive research considering these four areas has been conducted on the influence of external factors on the polymorphism and crystallization of lipids, such as using additives, shear, sonication, emulsification, or temperature variation. Applying such external influences may modify crystallization kinetics of lipids, so that the microstructures of lipid crystals and, ultimately, the functional properties of the end food product (e.g., texture and melting) may also be changed.

In this review, we briefly focus on the effects of such external factors as the application of dynamic temperature variation, template effects, shear, and emulsification to form water-in-oil (W/O) emulsion systems. For this purpose, we may focus on the recent research performed in the past several years since previous reviews [1-3].

For sonication effects on lipid crystallization, the readers should refer to a recent monograph [4] and research articles [5-8]. For the crystallization of lipid phases in oil-in-water (O/W) emulsion systems, recent research of nucleation kinetics of lipid crystals in oil droplets was reviewed by Povey [9]. Douaire et al. also reviewed recent advances in the research of lipid crystallization near water-in-oil interfaces with the aid of emulsifiers in the O/W and W/O emulsion phases [10].

Effects of dynamic temperature variations

The occurrence of metastable and more stable polymorphic forms of lipids is largely influenced by dynamic temperature variations such as the rates of cooling and heating. These effects can modify the occurrence of specific polymorphic forms by tailoring the most efficient thermal treatments, and such forms should be maintained over long periods by preventing their conversion into other less functional polymorphic forms.

The influence of thermal treatment on lipid crystals has recently been applied from single pure triacylglycerol (TAG) components [11-14] and their mixtures [15, 16] to end food products [17-21]. The effects of cooling and heating rates on the polymorphic behavior of TAG components have been related to some structural aspects, such as the chain length of fatty acid moieties and the symmetric/asymmetric structures of TAG molecules. Differences observed in kinetic crystallization have also been analyzed in lipid binary mixtures by considering molecular structures and interactions between component TAGs. For more complex systems, variations in the thermal treatment can largely determine final textural characteristics of the end food product, such as spreadability and mouthfeel, as reported on the polymorphism, microstructure, and rheology of butter [20-21]. Using different cooling rates resulted in similar polymorphic forms, but different microstructures of butter: butter produced from slowly cooled cream had a wider size distribution, whereas rapidly cooled cream resulted in more uniform crystals. The study of kinetic effects on the polymorphic crystallization of lipids may also provide valuable information for industrial applications improvement and optimization. In this sense, Rincón-Cardona et al. characterized the polymorphic behavior of sunflower oil fractions when different thermal treatments were applied to be used as trans-fat replacers and cocoa butter equivalents with optimized processing conditions [19].

The crystallization of lipid systems under non-isothermal conditions (variation of the cooling and heating rates) becomes quite complex due to the presence of different component TAGs and their multiple polymorphic forms. In order to monitor the polymorphic behavior in such dynamic conditions, synchrotron radiation X-ray diffraction techniques coupled to differential scanning calorimetry become extremely useful, as they enable rapid thermal programs to provide highly accurate structural information. By following this methodology, the effects of the cooling and heating rates on the nucleation and transformation of polymorphic forms have been studied for several TAGs [22-24]. In all cases, larger quantities of more stable forms were obtained when the samples were slowly cooled and heated, whereas less stable polymorphs predominated with increased cooling and heating rates. Polymorphic transformations occurred in either solid-state or melt-mediation and were influenced by heating rates.

Template effects of additives

The recent ban on using lipids containing *trans*-fatty acids has meant that the current and future development of lipid-based food products will have to rely more on the lipids without partly-hydrogenated fatty such as natural lipids with highly saturated lipid content (palm oil, coconut oil etc.). Since the crystallization rates of *trans*-lipids are inherently higher than those of non-hydrogenated lipids in the current scenario, more effort needs to be focused on exploring ways to hasten the process of lipid crystallization. The use of hydrophobic additives can be considered as one promising approach, because the additives are known to influence the bulk properties including consistency, texture, yielding force, solid lipid content, and post-hardening phenomena [25] in addition to promoting (or inhibiting in some cases) lipid crystallization (including nucleation, crystal growth, polymorphic transitions, and consequent morphology of crystals) [25-27].

The positive effect of hydrophobic additives on lipid crystallization is mostly attributed to the "templating effect," which simply refers to the phenomenon where a higher melting additive with significant structural and chemical similarities to the lipid (similarity in fatty acid composition, carbon chain length of acyl groups, saturation/unsaturation levels, polymorphic correspondence, and thermal stability) serves as a template (seeding nuclei) for heterogeneous crystallization of lipids. This results in earlier onset of crystallization because of the crystal nucleation at higher temperatures [28, 29], co-crystallization of additive and TAGs if the concentration of the additive is high enough [30], increased cut-off temperatures of lower polymorph formation by promoting the formation of more stable polymorphs [31], and fractional crystallization [30].

Recently, the templating effect of additive-monoplamitin on crystallization of palm oil was studied using a state-of-the-art synchrotron radiation microbeam X-ray diffraction (SR-μ-XRD) technique, and it was concluded that high-melting TAG crystals of palm oil were oriented by previously formed monopalmitin crystals that acted as templates due to their structural similarities with TAGs in palm oil [32]. Furthermore, the positive effect of polyglycerol fatty acid esters (PGFEs) on crystallization of palm stearin was also considered due to the templating effect [26]. When an additive is used above its equilibrium solubility concentration, it crystallizes ahead of the bulk lipid and promotes crystallization by serving as a template.

Interestingly, new findings have shown that inorganic (talc, carbon nanotube, and graphite) and organic (theobromine, ellagic acid dihydrate, and terephthalic acid) materials can also exhibit templating effects of lipid crystallization [33, 34]. Such additives have great potential for promoting lipid crystallization by both hydrophobic and hydrophilic molecular interactions between the lipids and additives.

Effects of shear

The application of shear increases the rates of polymorphic crystallization and transformation of lipids and modifies the aggregation of nanocrystals of the lipid crystal network, as fully reviewed in [2]. Further clarification of the effects of shear on crystallization and physical properties of lípid-crystal aggregates has been attempted from various viewpoints: combined effects of temperature variation and shear application [35], oil binding properties of fat blends of fully hydrogenated soybean oil in soybean oil [36-38], morphological changes of lipid crystals of fully hydrogenated canola oil blended with canola oil caused under shear at different cooling rates [39], improved physical properties of fat blends composed of soybean oil, coconut oil and palm stearin [40], and organogels [41] under high shear.

Since the first systematic work on shear effects, cocoa butter has been the most extensively examined lipid material. This is because (1) control polymorphism, morphology and network structures of cocoa butter crystals is a prerequisite to reveal snap, gloss, and sharp melting of chocolate, and (2) preceding research has shown that application of an optimal shear rate promotes the polymorphic crystallization in stable form and improves the crystal network of cocoa butter crystals [2]. Further studies have provided new information on the shear-induced cocoa butter crystallization behavior [42-45].

The rates of oil migration from liquid-oil-containing filling to chocolate were quantitatively assessed by crystallizing cocoa butter with and without shear [42]. Optical microscopy revealed that the secondary nucleation was promoted and cocoa butter crystals formed clusters under shear [43].

When shear was applied just below the melting point of form V, the crystallization of form VI has been detected. Therefore, the shear-induced polymorphic transformation of cocoa butter crystals would not be limited with the metastable form V but progress until the most stable form VI [44].

Water-in-oil emulsion droplets

Crystal-stabilized water-in-oil (W/O) emulsions are increasingly used in food and other applications ranging from controlled release applications [46, 47] to novel confectionery products [48, 49] and lipstick formulations [46, 50, 51]. Yet, the impact of a dispersed phase on fat crystallization remains virtually unexplored. For example, during the manufacture of table spreads such as margarines which typically exist as W/O emulsions, the presence of interfacially-active species on aqueous droplets may impact the nucleation and growth of TAGs in the surrounding bulk phase. Such exploration is relatively recent [52-55].

Continuing efforts are providing further evidence of interfacial templating at the surface of water droplets in W/O emulsions. Observation of the lipid crystals with a synchrotron radiation microbeam X-ray diffraction technique is quite useful for this purpose [56]. **Figure 2A** is a polarized light image of two water droplets surrounded by a hydrogenated fat/vegetable oil blend, with the surfactant glycerol monostearate (GMS) used given the structural similarity of its fatty acid moiety with that of the stearic acid chains in the hydrogenated fat. Both droplets are surrounded by a mixture of solid fat spherulites and surface crystallization, given the slight droplet deformation observed. **Figure 2**B is a close-up of the lower edge of Droplet 2 explored for interfacial crystal orientation, along with the regions scanned using synchrotron microbeam x-ray diffraction. **Figure 2**C presents the corresponding x-ray diffraction scans revealing a high degree of interfacial crystal orientation in squares 2-6 compared to squares 1 and 7 where little or no orientation is observed. Finally, **Fig. 2**D is a 3D representation of region 4 further emphasizing fat crystal alignment.

In the molten state, the GMS molecules will self-assemble at the water droplet surface during emulsification, resulting in a disordered interfacial brush arrangement, with its polar groups (hydroxyl and carbonyl groups) residing in the aqueous side of the interface and the acyl chains exposed to the oil phase. Presuming molecular complementarity, the fatty acid chains present in the surrounding TAGs will associate with those of the surfactant *via* van der Waals and hydrophobic interactions. Below their respective crystallization temperatures, the associated acyl chains in the GMS and

TAGs will undergo a *gauche-trans* transition leading to interfacial heterogeneous nucleation of the fat [57]. Templated crystal growth of highly-aligned TAGs at the oil-water interface will proceed as the crystals thicken, spread, and cover the entire droplet with a solid fat crystal shell. Given its importance to the texture and stability of fat-containing products, continuing efforts are necessary to fully clarify the mechanisms of interfacial lipid crystallization in W/O systems as well as its effects on morphology and polymorphism of lipid crystals.

Conclusion

Recent strong market demands, based on nutritional concerns, require reducing *trans* and saturated fatty acids in lipid-based food products. Despite this, functionality of the lipid crystals cannot be completely reproduced with other ingredients because various physical and chemical properties of sharp melting behavior, texture, retention of oil-soluble ingredients, stabilization of air bubbles etc. are specific to lipids containing saturated fatty acid moieties.

Basic and application research may thus be directed to the following areas: (1) exploring ways of enhancing the crystallization rates and strengthening the crystal network of low-saturated products by applying external factors influencing the crystallization of lipids, (2) finding alternatives to *trans*-fats and saturated-fats such as organogels, and (3) finding ways to hybridize "*traditional*" lipids and saturates-alternatives.

The present review has highlighted recent topics of (2) above, and we expect to develop further research in this and other areas in the near future.

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Figure legend:

Figure 1

Illustrations to relate external influences to crystallization of lipids

Figure 2

A) Polarized light image of a 20 wt% water-in-oil emulsion, with the oil phase consisting of 69 wt% canola oil, 10 wt% hydrogenated canola oil and 1 wt% glycerol monostearate. Size bar = 50 μm. B) Close-up view of the dotted rectangle in A). Squares 1-7 are the areas scanned via synchrotron microbeam X-ray diffraction. C) X-ray scans corresponding to squares 1-7 in B. Note clear evidence of oriented interfacial crystallization in scans 2-6 and lack thereof in images 1 and 7. D) 3-D view of scan region 4 further highlighting existence of orientation.

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Figure 1

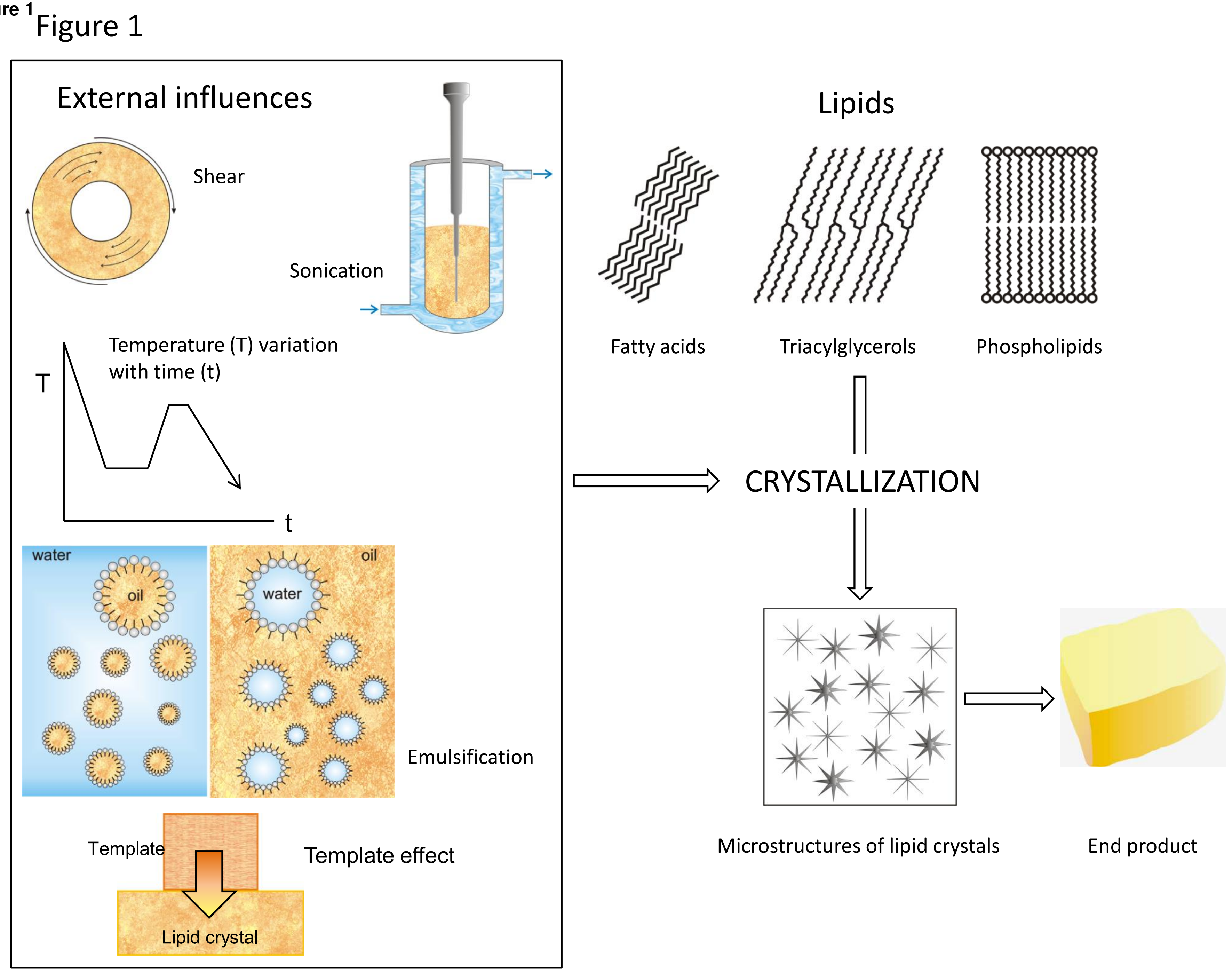

Figure 1
External influences
Shear
Sonication
Temperature (T) variation
with time (t)
T
t
water
oil
oil
water
Emulsification
Template
Template effect
Lipid crystal
Lipids
Fatty acids
Triacylglycerols
Phospholipids
CRYSTALLIZATION
Microstructures of lipid crystals
End product

Figure 2
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