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ABSTRACT

Confections such as chocolate and biscuit fillings are composed of a continuous fat phase that contains dispersed nonfat ingredients such as sugar and cocoa powder. Research on fat crystallization and rheology in confections often extrapolates crystallization and textural properties from bulk to mixed systems while overlooking the important role of composition or particle interactions. For example, in chocolate processing the fat phase aids dispersed phase lubrication and fluidity whereas the dispersed particles assist in fat crystallization by providing many nucleation sites. In confections with a high dispersed phase volume fraction, fat crystallization may be hindered due to reduced triacylglycerol mobility, confinement, and increased tortuosity. This is further complicated in systems with slow crystallizing fats such as palm oil whose crystallization is exceptionally sensitive to composition and processing. This review breaks down the physical chemistry of fat-based confections and discusses the impact of different nonfat ingredients towards fat crystallization and rheology. The behavior of palm oil is further highlighted as it is becoming increasingly popular as a confectionery ingredient. Lastly, ingredient-ingredient interactions and their role in fat crystallization are described along with force spectroscopy as a novel tool to characterize such phenomena. Force spectroscopy utilizes atomic force microscopy to measure intermolecular forces as a function of distance but remains largely unexplored in the area of food science.

Abbreviations: PO: palm oil; CB: cocoa butter; MF: milkfat; TAG: triacylglycerol; DAG: diacylglycerol; MAG: monoacylglycerol; FA: fatty acid; FFA: free fatty acid; PGPR: polyglycerol polyricinoleate; φ: volume fraction of nonfat ingredients; q: cooling rate; T_e: cooling endpoint; SFC: solid fat content; AFM: atomic force microscopy; PLM: polarized light microscopy; XRD: x-ray diffraction; DSC: differential scanning calorimetry; γ: shear; τ_0: yield stress; η^*: viscosity

1. Fat-based confections

1.1 Main components

Processed foods are composed of numerous ingredients often existing in a multi-phasic environment with structures ranging from the nano- to the macro-scale (Rao, 2007; Walstra, 2003). In fat-based confections, nonfat ingredients such as sugar, salts, cocoa solids, and/or proteins are dispersed within a continuous semi-solid fat phase (Afoakwa et al., 2009; Carvalho-da-Silva et al., 2013; Dahlenborg et al., 2011; Götz et al., 2005; Sokmen and Gunes, 2006; Svanberg et al., 2013), whose fat crystal morphology, polymorphic behavior, and interactions with nonfat ingredients determine processability, quality, and sensory properties of the final product (Fig. 1). Chocolate, which is perhaps the most popular and well-studied of these confections, is solid-like at room temperature ($\leq 25°C$), but melts sharply once in the mouth (33–38°C) (Afoakwa et al., 2008a). The proper crystallization of cocoa butter (CB), which can account for up to 30–40 wt.% of the product, is largely responsible for the sensory behavior that consumers have come to expect (Afoakwa et al., 2007a; Fernandes et al., 2013; Rousseau, 2007).

Often, the main ingredient of fat-based confections is sucrose (Beckett, 2000; Krüger, 1999), which provides sweetness and mouthfeel (Jamieson, 2008) and is also a source of energy (4 kcal·g^{-1}) (Aidoo et al., 2013). Adjusting the sugar content by as little as 5 wt.% can significantly impact the perceived sweetness in some food applications (Beckett, 2008). In products such as chocolate, optimal sugar particle size is approximately 30 μm in diameter in order to maintain proper textural properties (Jeffery, 1993). Coarser particles tend to confer proceegrittiness while finer particles impact fluidity (Beckett, 2000). A particle size distribution of 60% coarse and 40% fine particles has been shown to minimize the melt viscosity of fluid chocolate (Servais et al., 2002).

Emulsifiers are added to confections to lubricate and aid in the dispersion of sugar and other nonfat ingredients within fat-continuous environments (Afoakwa et al., 2007a; Beckett, 2000; Götz et al., 2005; Van Der Vaart et al., 2013). The most commonly used emulsifiers are soy lecithin, which contains phospholipids that contribute to its amphiphilic properties, and polyglycerol polyricinoleate (PGPR), a synthetic equivalent that shows a greater reduction in confectionery yield stress than lecithin (Schantz et al., 2003; Vernier, 1998). Other nonfat ingredients commonplace in confections includes milk solids, which are composed of casein and whey proteins, that have traditionally been added to provide a 'creaminess' (Haylock and Dodds,
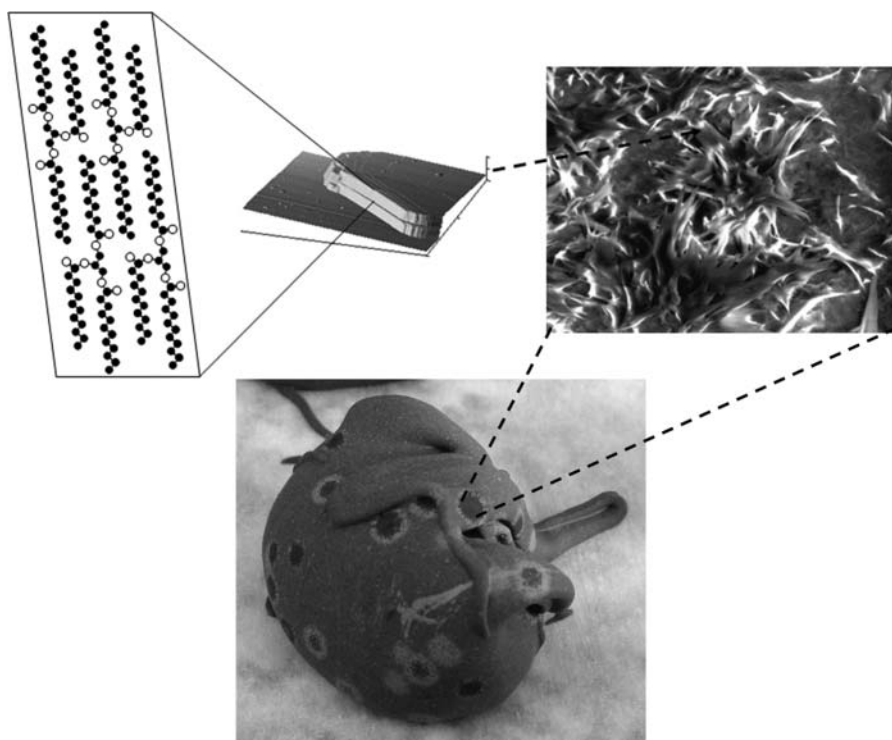
Figure 1. Multiscale interpretation of chocolate from glyceride assembly to fat bloom.

1999), and cocoa solids, which contribute to flavor, texture, and are a source of antioxidants (Doká et al., 2013).

1.2 Rheology

This section summarizes the role of key ingredients found in confections on rheology, including the fat phase, sucrose, milk proteins, cocoa powder, and emulsifiers. The rheological properties of foods are important given their close association with processing efficiency, e.g., extrusion, enrobing, etc., and organoleptic properties (Ahmed and Ramaswamy, 2006; Baixauli et al., 2007; Denker et al., 2006; Engelen and Van Der Bilt, 2008; Engelen et al., 2005; Kilcast and Clegg, 2002; Liu et al., 2010; Servais et al., 2002, 2004; Zarić et al., 2012; Ziegleder, 2009). Oscillatory rheology is used to explore confectionery fat crystallization in the absence of shear (γ), i.e., under conditions where the material is not irreversibly deformed (De Graef et al., 2006; Omar et al., 2005). By contrast, rotational rheology explores the influence of both torque and rotational shear on material properties such as viscosity (η^*), for example during the conching of dark chocolate (Vivar-Vera et al., 2008).

The rheological properties of confections depend on the physical properties of the continuous fat phase, e.g., solid fat content (SFC), crystal morphology, etc., the volume fraction of nonfat ingredients (φ), and specific ingredient interactions (Bouzas and Brown, 1995; Do et al., 2007; Jeffery, 1993; Kulozik et al., 2003; Liang and Hartel, 2004; Pérez-Martínez et al., 2007; Rao, 2007; Schantz and Rohm, 2005; Sokmen and Gunes, 2006; Tang and Marangoni, 2007; Tscheuschner, 1994; Tscheuschner and Wünsche, 1979; Van Den Tempel, 1979).

Fat-based confections are often shear-thinning, non-Newtonian pseudoplastic materials, possessing a measurable yield stress (τ_0) (Chabbra, 2006; Chevalley, 1999; Rector, 2000; Schantz and Rohm, 2005). Reduction of the continuous phase volume, as seen in fat-reduced products, results in a harder, more brittle texture (Beckett, 1999; Spearing, 2007). In fat reduced dark chocolate, viscosity has been shown to increase as a result of the reduced lubrication of sugar and other non-fat ingredients (Afoakwa et al., 2007b). In contrast, the addition of continuous phase results in a smoother, more fluid product (Aidoo et al., 2012) and plateaus at 32 wt.%, above which no effect is seen (Afoakwa et al., 2007a). The proportion of fat used in confections must also be considered during processing because of its impact on pumping, moulding, and other unit operations (Do et al., 2008). For example, chocolate may be pumped within pipelines at a flow rate of 10 t·h^{-1} across several dozens of meters within a production setting (Walker, 2009). Complications due to fat-reduced formulations, such as increased hardness and difficulty to swallow (Beckett, 1999; Spearing, 2007), have been circumvented by either increasing emulsifier content or the addition of CB replacers (Wang et al., 2010), oleogels (Kaiser et al., 1998; Marangoni, 2012), or limonene (Beckett, 1999; Do et al., 2008), all of which help to maintain proper rheology.

The φ and their particle size distribution strongly impact rheology. Importantly, surface area and interactions with the continuous phase increase with a reduction in particulate size as this increases the energy barrier needed to overcome τ_0 and results in a much higher η^* (Beckett, 1994; De Graef et al., 2011; Fernandes et al., 2013; Mongia and Ziegler, 2000; Walstra, 2003; Ziegler et al., 2001). For the consumer, this is perceived as increased hardness and decreased spreadability (Afoakwa et al., 2007b; Afoakwa et al., 2008b; Beckett, 2000; Chevalley, 1999). Hence, control of particulate size is critical in order to maintain rheology and prevent undesirable texture

attributes such as coarseness or grittiness (Afoakwa et al., 2007a; Jeffery, 1993; Servais et al., 2002).

Many commonplace ingredients will greatly contribute to the rheology of fat-based confections. Emulsifiers aid in processability and minimization of raw materials costs by improving the flow properties of chocolate and vegetable fat-based suspensions (mostly used as coatings) thorough lowering the friction between the particulates suspended in the liquid fat phase. As a result, τ_0 is reduced and ease of flow of these suspensions is permitted, even at low total fat content.

Using a sugar crystal as an example, to coat dispersed particulates, the hydrophobic moiety of the emulsifier will protrude into the fat phase whereas its hydrophilic moiety will adsorb onto the surface of the sugar crystal. In general terms, surface activity from an emulsifier will depend on chemical structure, namely the balance in size between the hydrophilic headgroup and hydrophobic tailgroup. Those with larger headgroups will bind more strongly to sugar whereas others will be less strongly attached and may even be removed by the addition of different emulsifiers. Similarly, tailgroup length may affect the flow properties in different ways, implying that emulsifiers that are especially beneficial with regard to τ_0 may be poor with respect to η^* and vice versa (Beckett, 2008).

Lecithins are derivatives of sn-glycero-3-phosphates with one or two fatty acid residues attached to a glycerol backbone and an alcohol esterified to a phosphate group at the third glycerol position. They are commonly used to stabilize particulates in oil-continuous dispersions (e.g., sugar particles in CB), as they align into layers at the solid surface to reduce η^* stemming from particle aggregation (Johansson and Bergenståhl, 1992). For example, in chocolate manufacture, cocoa liquor (or mass) is mixed with sugar, additional CB, milk powder, and lecithin and through refining and conching the action of shear and coating of sugar with fat and lecithin improves chocolate flow properties. The addition of soy lecithin decreases τ_0 and η^* in chocolate until a maximum concentration of 4 g·kg^{-1}. Beyond this point, continued addition begins to increase τ_0 (Table 1) (Chevalley, 1999; Schantz and Rohm, 2005). This is attributed to the micelles produced from lecithin phospholipids that disrupt particulate flow (Vernier, 1998).

PGPR is a synthetic food-grade emulsifier consisting of polyglycerol as the hydrophilic group and interesterified ricinoleic fatty acids as the hydrophobic group (molar mass between 1200–2000 g·mol^{-1}) (Middendorf et al., 2015). It is increasingly being sought as a replacement for lecithin given its η^*-reducing effects that are generally similar to lecithin but at lower wt.% values. For example, Ghorbel et al. (2011) found PGPR

decreased τ_0 more significantly than either lecithin or total fat content in molten milk chocolate. Both emulsifiers had similarly influenced η^*. The interaction between emulsifier and fat on the one hand—and those between the emulsifier and solid particles on the other hand—play an important role not only in determining chocolate flow properties but also texture of the final product. Rousset et al. (2002) stated that PGPR enhanced the lipophilicity of sugar particles thereby decreasing sugar–sugar interactions and increasing the fluidity of the fat-based suspension. Finally, Middendorf et al. (2015) concluded that PGPR interacts with CB immobilized on the surface of sugar in order to form pillow-like deposits, which act as spacers to reduce interaction between sugar particles. In addition to providing creaminess, milk solids also impact rheology where casein, which possesses both polar and nonpolar sites, behaves similar to an emulsifier (Haylock and Dodds, 1999).

An increase in demand of low-calorie confections has resulted in many sugar-free products (Sokmen and Gunes, 2006; Zumbé and Brinkworth, 1993). Sugar substitutes, which include bulk sweeteners such as sugar alcohols, e.g., sorbitol and xylitol, and saccharide alternatives, e.g., trehalose and isomaltulose (Aidoo et al., 2013; Kroger et al., 2006; Olinger, 1994), have a negative impact on rheology (Clayton and Conn, 2005). For example, sugar alcohols were found to reduce the quality of chocolate and result in poorer rheology (Zumbé and Brinkworth, 1993). A further study showed that maltitol produced a η^* most similar to sucrose whereas isomalt significantly increased it (Sokmen and Gunes, 2006). In another study, the substitution of sucrose with steviol glycosides, which are natural sweet-tasting compounds isolated from the plant *Stevia rebaudiana*, in combination with inulin and dextrose as bulking agents was found to not significantly alter hardness of chocolate (Shah et al., 2010).

Moisture often has a dire effect on fat-based confections. It causes dispersed particulates to cluster through attractive polar forces and capillary action, resulting in poor mixing and increased particle heterogeneity as well as deleterious effects on η^* (Nováková et al., 2002). This is in large part due to the low affinity sugar has for the continuous phase. The effect of moisture has also restricted the usage of hygroscopic low-calorie ingredients such as glucose or fructose (Afoakwa et al., 2007a). To counteract this effect, confections are formulated with a higher fat content, though this is clearly not cost-effective. For example, CB is adjusted by a three-fold addition for every one-fold addition of unwanted moisture in order to correct its rheology (Aidoo et al., 2012; Beckett, 2000). Approaches such as high intensity conching (Nováková et al., 2002) and ultrasound (Yucel and Coupland, 2011) may also remove these aggregates.

A nascent area is that of the role of micro-viscosity and rheology on particle networks. In particular, characterizing the micro-rheological properties of liquid-state oil may improve our understanding of the role of confinement and nonfat ingredient interactions on fat crystallization. Therefore, it is important to isolate this behavior from the aforementioned bulk rheology as much as possible. It was previously reported that the micro-viscosity of localized oil was influenced by the fractal dimension of fat-oil mixtures and not their SFC. Relying on the twisted intramolecular charge transfer properties of the molecular rotor citrus red, micro-viscosity was determined to

Table 1. Effect of soy lecithin concentration on τ_0 and η^* of milk chocolate (Schantz and Rohm, 2005).

Concentration (g·kg^{-1})	τ_0 (Pa)	η^* (Pa·s)
0	79.60	12.30
1	19.50	4.18
2	11.80	3.63
3	10.20	3.28
4	9.00	3.04
5	9.15	2.89
6	9.59	2.79
7	10.30	2.71

increase as oil confinement and fractal dimension increased (Du et al., 2014). While determination of oil micro-viscosity may possibly give insight into its migration and impact on crystallization in systems containing nonfat ingredients, any existing study remains to be published.

Large deformation experiments, e.g., cone penetrometry and two-plate compression, are used to determine the textural properties of foods, e.g., mechanical firmness and adhesiveness, and are often used to corroborate sensory tests (Hayakawa and DeMan, 1982; Liang and Hartel, 2004; Omar et al., 2005; Rousseau and Marangoni, 1999). These experiments may also be used in conjunction with rheology (Beckett, 2000; Bourne, 2002). The main limitation with texture analysis is the inability to reproduce chewing and the absence of saliva, which can invert phases within fat-based confections, changing the way in which they are perceived (Carvalho-da-Silva et al., 2013; Lee and Pangborn, 1986). Tribology, which studies the interaction between food and oral epithelia, has been developed to minimize this challenge. The tribological properties of some fat-based confections have been studied, though much work remains to be done in this area (Carvalho-da-Silva et al., 2011; Lee et al., 2002).

2. Fats and oils

2.1 Molecular structure

Like all food fats, confectionery fats are mixtures of solid- and liquid-state triacylglycerols (TAGs) where fatty acids (FAs) are esterified to a glycerol skeleton (Fig. 2) (Timms, 1984). These molecules conform to an asymmetric tuning fork or chair geometry due to steric hindrance at the sn-2 position (Larsson et al., 2006). Hindrance is exacerbated with unsaturation at this position, e.g., oleic acid in CB TAGs, which is partly responsible for its sharp melting behavior (Afoakwa et al., 2007a; Smith and Dahlman, 2005).
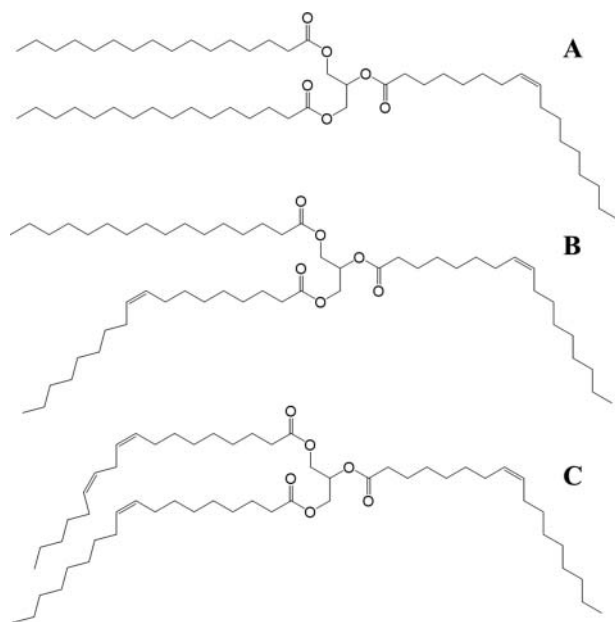
Table 2. Effect of CB origin on TAG composition (Marty and Marangoni, 2009).

TAG (%)[*]	Brazil	China	Ecuador	Ivory Coast	Malaysia	Nigeria
OOL	0.5	1.0	1.1	0.6	1.0	1.8
PLP	1.5	1.1	1.3	1.5	1.2	1.1
OOO	5.1	0.8	1.9	1.8	1.4	1.2
POP	22.8	23.5	24.1	24.3	22.7	23.1
PPP	0.0	0.1	0.0	0.0	0.0	0.1
SOO	7.0	1.7	2.1	2.1	1.8	1.2
POS	34.1	37.0	37.3	37.3	36.9	37.3
PPS	0.1	0.2	0.1	0.1	0.1	0.2
SOS	28.3	33.1	31.1	31.4	33.4	32.5
SSP	0.1	0.4	0.3	0.3	0.4	0.5
SSS	0.6	1.0	0.8	0.7	1.1	1.1

[*]Oleic (O), linoleic (L), palmitic (P), and stearic (S)

Mixtures of fats may be simple, consisting of just a few key TAGs, e.g., CB (Beckett, 2000; Loisel et al., 1998; Sato et al., 1989; Smith and Dahlman, 2005), or complex with several hundreds, e.g., milkfat (MF) (Gresti et al., 1993). As composition becomes more complex, the thermal profile of the fat becomes less defined and broader, e.g., MF melts between −40°C and 40°C (Larsson, 1994). Both origin and environmental factors, e.g., temperature and rainfall, can alter the composition of the source, influencing physical properties of the fat (Table 2) (Marty and Marangoni, 2009; Timms, 2003).

Common minor components include partial acylglycerols, e.g., monoacylglycerols (MAGs) and diacylglycerols (DAGs), free fatty acids (FFAs), and other components, e.g., carotene, tocopherol, etc. (Gee, 2007; Gibon et al., 2007; Kellens et al., 2007; Smith et al., 2011). DAGs have higher slip points than TAGs, which can negatively impact the intended application (Ab Latip et al., 2013). For example, in one study the slip points of commercial and DAG-enriched margarines were determined to be 30.5±0.2°C and 35.5±0.1°C, respectively (Saberi et al., 2012). With the consideration of oral temperature, a DAG-enriched margarine would have a longer, waxier thermal profile. DAGs are also believed to slow fat crystallization, although this mechanism is not fully understood (Siew and Ng, 1999; Tshiamala, 2013). Though emulsifiers are a mainstay of the fat and oil industry, there remains a dearth of information on their structure-function relationship and the mechanisms by which they influence TAG nucleation and growth. In this regard, they may significantly impact fat nucleation, crystal growth or both, depending on their composition, added amount and mechanism of action (Smith et al., 2011).

2.2 Polymorphism and morphology

The key polymorphs identified in most fats and oils, in order of increasing stability, are the α – hexagonal, β' – orthorhombic,

Figure 2. Molecular structure of (A) 1,3-dipalmitoyl-2-oleoylglycerol, (B) 1-palmitoyl-2,3-dioleoylglycerol, and (C) 1-palmitoyl-2-oleoyl-3-linoleoylglycerol.

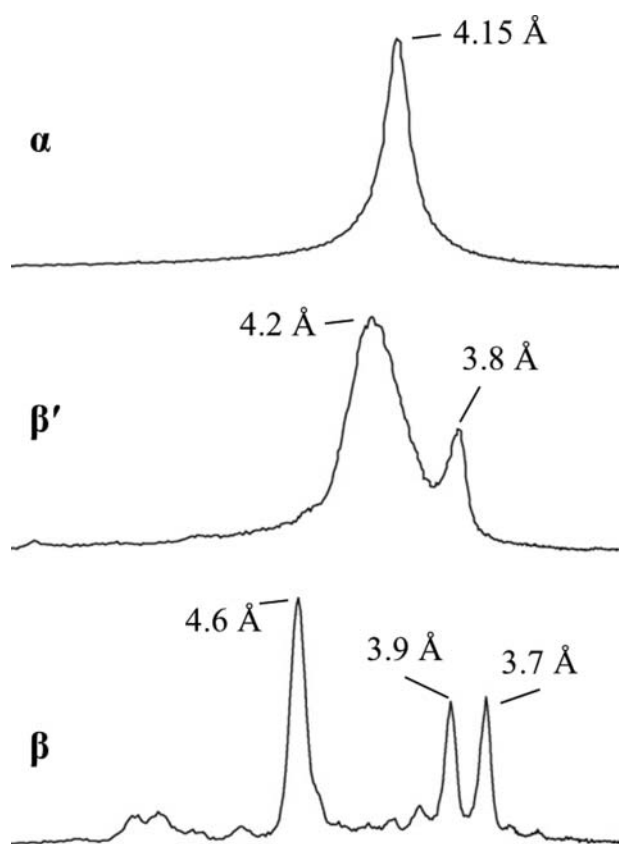**Figure 3.** Polymorphic forms of TAGs (Bresson et al., 2011).

Figure 4. Diffractograms of different tristearin polymorphs (adapted from Da Silva et al., 2009).

and β – triclinic forms (Fig. 3) (Bresson et al., 2011; Talbot, 1999; Tshiamala, 2013). These different packing configurations describe the lateral packing of molecules and provide the fingerprint short spacings. While polymorph subtypes have been reported in pure TAG systems, e.g., sub-α, pseudo-β', sub-β, etc., they are not universally accepted (D'Souza et al., 1990).

X-ray diffraction (XRD) is used to identify fat crystal polymorphs (Fig. 4) (D'Souza et al., 1990; Da Silva et al., 2009; Schenk and Peschar, 2004). With wide-angle XRD, the simplest definition is based on short spacings where one strong peak at 4.15 Å is observed for α crystals, peaks at 3.8 Å and 4.2 Å for β' crystals, and one strong peak at 4.6 Å and two lesser peaks at 3.7 Å and 3.9 Å for β crystals (DeMan, 1992; Hernqvist, 1988a; Larsson, 1966; Verstringe et al., 2012). These forms are driven by van der Waals forces to further pack into bilayer or trilayer lamellae two to three alkyl chains thick, respectively, interpreted as the long spacing of the crystals (Larsson et al., 2006; Talbot, 1999).

Other than XRD, many techniques can be used to characterize the crystallization behavior of fats (Loisel et al., 1998; Van Langevelde et al., 2001, 2001a; Van Malssen et al., 1994, 1999b), including differential scanning calorimetry (DSC) (De Cock, 2011; Foubert et al., 2008; Tshiamala, 2013), Raman spectroscopy (Bresson et al., 2005, 2006, 2011; Kobayashi, 1988; Da Silva et al., 2009; Hu et al., 2005; Schoukens and De Clerck, 2005), and dilatometry (Wille and Lutton, 1966) although this final technique is rarely used nowadays.

Polymorphs are associated with specific fat crystal morphologies under static crystallization. For example, α crystals are least dense and form platelets ~ 5 μm in length (Rousseau et al., 2005). Both β' and β crystals are acicular where crystal growth is more energetically favored along its length. These needle-like crystals are typically 1–2 μm and 50 μm in length for β' and β, respectively. Morphology may affect textural properties of bulk fats and oils. Rounded crystals, such as those shaped by shear, will flow past each other more easily to produce a smoother texture whereas sharper, more angular crystals will fracture and become brittle. For example, the ideal textural properties for palm-based margarines, including proper smoothness and spreadability, are obtained if β' crystals are formed. In more complex foods, the effect of crystal morphology on texture is not fully understood because of factors such as multiple phases, ingredient interactions, and compartmentalization (Hartel, 2001).

As in other fats, polymorphism in confectionery fats is monotropic evolving from less to more stable polymorphs. CB polymorphism has been studied extensively because of its close association to organoleptic properties and shelf life. A previous XRD study (Wille and Lutton, 1966), later to be confirmed by DSC (Huyghebaert and Hendrickx, 1971), showed a total of six polymorphs to exist in CB, i.e., γ, α, β'_2, β'_1, β_2, and β_1, melting over a range of 17 to 36°C (Table 3), with β_2 crystals exhibiting optimal macroscopic properties (Smith and Dahlman, 2005). The triple chainlength packing of higher order polymorphs further allows for higher thermodynamic stability and lower occupied volume compared to double chainlength packing (Talbot, 1999). With proper tempering, β_2 crystals initially form at 1–3 vol.%, establishing a template for further crystallization of the remaining melt (Svanberg et al., 2013). More contemporary methods use pre-made β_2 crystals to seed the melt and facilitate proper crystallization of the chocolate mass (Windhab, 1999; Zeng, 2000). Svanberg et al. (2011a) showed that seeded samples of molten chocolate formed multiple nucleation sites and a large degree of homogeneity was not observed in the absence of seeding. Instead, large spherical crystals were observed in some areas, but absent in others.

Importantly, β_2 crystals contribute to a glossy finish, clean fracture, i.e., snap, quick melting at oral temperature, flavor release, and contraction for demoulding of shelled confections (Beckett, 2000, 2008; James and Smith, 2009; Khan and Rousseau, 2006; Seguine, 1991; Stapley et al., 1999; Talbot, 1999; Timms, 1984, 2003). Shelf life is also prolonged because of the ability for β_2 crystals to restrict liquid oil from migrating to the surface and promote fat bloom, characterized by the onset of large β_1 crystals, i.e., > 5 μm, that have the ability to diffuse light, giving a dull, grey appearance of the surface (Cebula and Ziegleder, 1993; Dahlenborg et al., 2011; Dibildox-Alvarado et al., 2004; Glicerina et al., 2013; Hartel, 1999;

Table 3. Melting point and chain-length packing of CB polymorphs (Afoakwa et al., 2007a).

Polymorph	Melting point (°C)	Chainlength
γ	16–18	2
α	21–22	2
β'_2	25.5	2
β'_1	27–29	2
β_2	34–35	3
β_1	36	3

Lohman and Hartel, 1994; Loisel et al., 1997; Lonchampt and Hartel, 2004; Nopens et al., 2008; Sato, 2001; Smith et al., 2007; Timms, 2003; Ziegleder, 1997). Furthermore, with β_1 crystals, melting point is increased and the product adopts a gritty texture (Afoakwa et al., 2009). Internally, β_1 crystals may also form but are typically smaller and more irregularly shaped (Dahlenborg, 2014; Dahlenborg et al., 2011; Hartel, 1999; James and Smith, 2009; Jewell, 1972; Lonchampt and Hartel, 2004). With proper storage, it may take years for properly-tempered chocolate to produce enough bloom-inducing β_1 crystals (Bomba, 1993; Rousseau et al., 2010; Subramaniam, 2000). With under-tempering, this process occurs in just days (Bresson et al., 2011; Campbell, 1967; Hernqvist, 1988b; Rousseau, 2007; Vaeck, 1960), as β'_1 crystals rapidly form due to the lack of a proper template and undergo a $\beta'_1 \rightarrow \beta_2$ transition on the surface of chocolate (Hodge and Rousseau, 2002; Schlichter-Aronhime and Garti, 1988; Seguine, 1991).

2.3 Crystallization

Fat crystallization may occur from either melts or solutions (Fig. 5) (Himawan et al., 2006; Kellens et al., 2007). This process is driven by the reduction of activation free energy as the system is shifted from equilibrium and either the melt is cooled

Figure 5. Timeline of events during fat crystallization and storage (adapted from Himawan et al., 2006).

below its melting point or the solution has reached saturation. For melts, the chemical affinity (Φ), which is the driving force promoting TAGs to associate, is expressed by:

$$\Phi = \Delta H_f \frac{(T_f - T)}{T_f} \qquad (1)$$

where ΔH_f is the latent heat of fusion, T_f is the melting point, and T is the temperature of the system (Hartel, 2001). For solutions, this is expressed by:

$$\Phi = RT \ln\left(\frac{\gamma X}{\gamma_s X_s}\right) \approx RT \ln\left(\frac{C}{C_s}\right) \qquad (2)$$

where R is the gas constant, γ is the activity coefficient, γ_s is the activity coefficient at equilibrium, X is the mole fraction, X_s is the mole fraction at equilibrium, C is the concentration, and C_s is the saturation concentration (Hartel, 2001). Obviously, as T is reduced in either melts or solutions, so is Φ. In systems of great TAG diversity, crystallization proceeds from both melt and solution. This is explained by the presence of lower-melting TAGs serving as solvent for fat crystals composed of higher melting TAGs. Butter is just one example of a mixed system where crystallization from both melt and solution occurs (Hartel, 2001).

The first step in crystallization is primary nucleation where molecules either combine from the molten state, i.e., homogeneous, or form on the surfaces of impurities, i.e., heterogeneous (Basso et al., 2010; Metin and Hartel, 2005). Liquid-state TAGs assemble through local energy fluctuations into embryos under homogeneous nucleation (Mullin, 1993; Walton, 1969; Zettlemoyer, 1969). This process is reversible but the rate of association eventually exceeds that of dissociation as the system continues to shift away from equilibrium. These embryos must form prior to the formation of stable nuclei of a critical size. For melts, this critical size (r_c) is estimated by:

$$r_c = \frac{2\sigma_s \nu T_f}{\Delta H_f (T_f - T)} \qquad (3)$$

where σ_s is the interfacial tension and ν is the molecular volume (Hartel, 2001). The rate of homogeneous nucleation (J_{hom}) from the molten state is:

$$J_{hom} = A \exp\left\{\frac{16\pi\sigma_s^3 \nu^2 T_f^2}{3kT\Delta H_f^2 (T_f - T)^2}\right\} = A \exp\left\{-\frac{\Delta G_c}{kT} + \frac{\Delta G'_\nu}{kT}\right\} \qquad (4)$$

where k is Boltzmann's constant, ΔG_c is the critical free energy for a stable nucleus, and $\Delta G'_\nu$ is the free energy for molecular diffusion. Nucleation is further influenced by polymorphism where the rate increases with lower order (Hartel, 2001). A reduced σ_s in α crystals is one suggestion behind their tendency to nucleate before either β' or β crystals (Sato, 1988), where their greater chain mobility may significantly reduce interface energy.
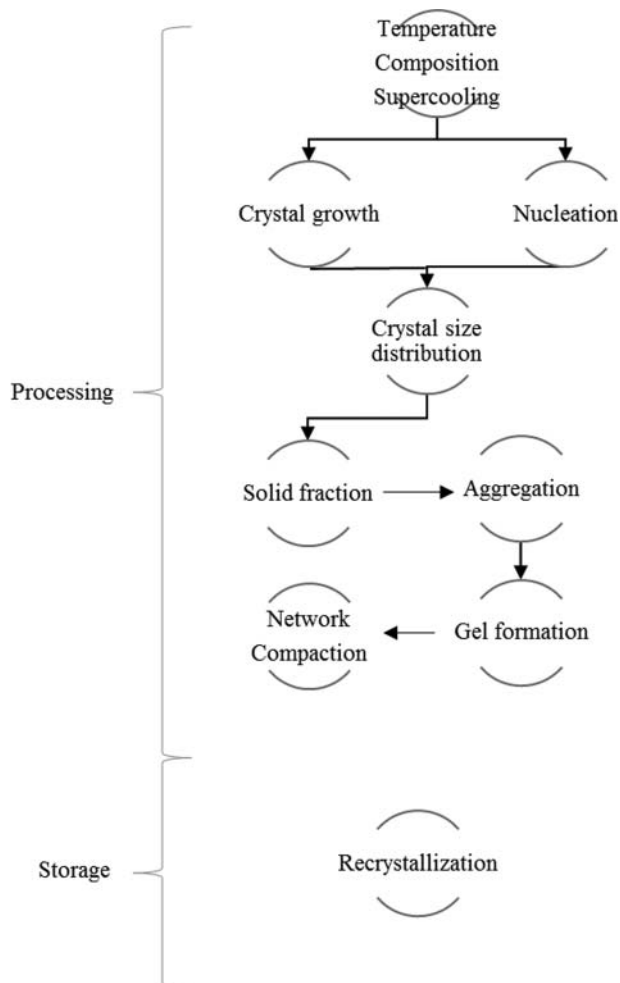
The theory behind heterogeneous nucleation (J_{het}) is a modification of homogeneous nucleation, such that:

$$J_{het} = A \, exp\left\{ - \frac{\Delta G_c^{'}}{kT} \right\} \qquad (5)$$

where $\Delta G'_c$ is the critical free energy for heterogeneous nucleation (Hartel, 2001). $\Delta G'_c$ in this case is the combination of tensions at the melt-foreign surface, crystal-foreign surface, and melt-crystal interfaces (Garside, 1987). $\Delta G'_c$ may be explained by:

$$\Delta G_c^{'} = \Delta G_c\left\{\frac{1}{4}(2 + cos\theta)(1 - cos^2\theta)\right\} \qquad (6)$$

where θ represents the angle of wetting between crystal and nucleating solid. This angle may be calculated by:

$$cos\theta = \frac{\sigma_{sl} - \sigma_{cs}}{\sigma_{cl}} \qquad (7)$$

where interfacial tensions for melt-foreign surface, crystal-foreign surface, and melt-crystal are σ_{sl}, σ_{cs}, and σ_{cl}, respectively. The presence of a foreign surface, such as a sugar particle, should lower θ, which in turn requires fewer liquid-state TAGs to assemble a nucleus of critical size. In return, $\Delta G'_c$ is lowered and nucleation occurs more easily (Hartel, 2001). Furthermore, a greater degree of lattice matching, i.e., physical or chemical complementarity, between the foreign surface and fat crystal impacts nucleation of the system (Metin and Hartel, 2005).

Foreign surfaces that facilitate nucleation may be inherent to the system, e.g., dust, dirt, etc., or they may be intentionally added. For example, heterogeneous nucleation of fat crystals off the surface of sugar particles was observed in nonseeded CB-sugar systems (Svanberg et al., 2011a). It has been theorized that one catalytic impurity per cubic millimeter results in a nucleation large enough to ensure rapid phase transition at a given supersaturation (Walstra, 2003). Homogeneous nucleation rarely proceeds in food systems because of this (Cacciuto et al., 2004; Eremina et al., 2005; Land et al., 1999; Rak et al., 2005).

The deviation from equilibrium required for nucleation is reduced in the presence of foreign surfaces because they provide active sites that lower the energy barrier by facilitating proper orientation of liquid-state TAGs (Bowser, 2006; Fernandes et al., 2013; Hartel, 2013; Rousseau and Sonwai, 2008; Svanberg et al., 2011, 2011ab). For example, crystallization induction time is reduced in the presence of sugar for palm oil (PO) (Fig. 6), cocoa solids for CB (Svanberg et al., 2011a), common minor components of fats and oils (Savage and Dimick, 1995), and solvents such as acetone (Hartel, 2001). Furthermore, local shear rates near nonfat ingredient surfaces increase nearly two-fold, providing enough energy to promote transition to higher ordered polymorphs (Dhonsi and Stapley, 2006; Mazzanti et al., 2003). The effect of various lipophilic molecules on nucleation has been previously reviewed (Smith et al., 2011; Yoshikawa et al., 2014).
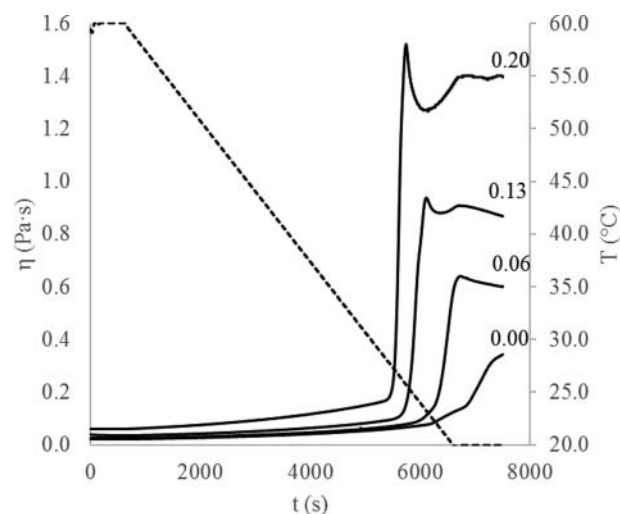

Figure 6. Effect of sugar volume fraction on PO crystallization during cooling (unpublished data).

The effect of inorganic additives on trilaurin (LLL) crystallization was recently studied by Yoshikawa et al. (2014). These additives appeared to enhance crystallization and the $\beta' \rightarrow \beta$ transition. Furthermore, there existed an interaction between type of additive and TAG orientation on the surface of LLL crystals. XRD studies revealed greater peak intensities for long spacing over short spacing in the presence of talc, suggesting orientation where lamellar planes were parallel to additive surface. In contrast, these planes grew normal to the surface of graphite (Fig. 7) (Yoshikawa et al., 2014). Crystallization suppression may sometimes be observed in the presence of an additive (Cacciuto et al., 2004). For example, lecithin has suppressed fat crystallization of CB-sugar models (Dhonsi and Stapley, 2006).

Crystals are fewer but larger in size if nucleation is slow, hindering their ability to flow across each other with minimal friction and causing products to become grainy or coarse in texture. For example, the textural quality of margarines is significantly reduced if crystals exceed 10 μm (Walstra, 2003). In contrast, high nucleation rates result in many smaller crystals and a pasty consistency (Hartel, 2001). The rate of nucleation may be quantified by refractive index, turbidimetry, or light scattering although this has been met with challenges (James, 1982).

Secondary nucleation depends on the presence of existing fat crystals and can occur in parallel to primary nucleation (Basso et al., 2010; Larson, 1981; Metin and Hartel, 2005). While questions remain as to how exactly this occurs (Randolph and Larson, 1988), some mechanisms suggest secondary nucleation
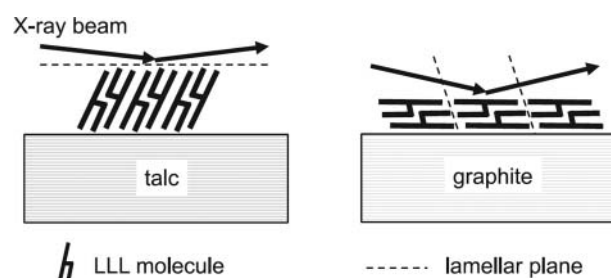

Figure 7. Effect of additive on lamellar orientation of LLL (Yoshikawa et al., 2014).

proceeds by micro-attrition where primary crystals fragment under high shear, feeding the secondary nuclei (Walstra, 2003). Following primary and secondary nucleation and crystal formation is crystal growth where liquid-state TAGs continue to incorporate onto crystal surfaces and heat of fusion is absorbed until an equilibrium is reached (Hartel, 2001, 2013; Tavare, 1995). The energy that is released from heat of fusion may also facilitate the transition of lower order crystals into higher states. Eventually these crystals agglomerate to form a network in which the remaining liquid phase is entrapped (Kellens et al., 2007; Metin and Hartel, 2005).

Following the formation of stable nuclei, growth and association of crystallized lamellae result in the formation of crystal nanoplatelets (Acevedo and Marangoni, 2010; Acevedo et al., 2011; Marangoni and Wesdorp, 2013). These CNPs organize into stack-like structures by means of molecular van der Waals forces which then go on to assemble into crystallites that cluster via colloidal van der Waals forces to form crystals. Aggregation and sintering (formation of solid bridges) between crystals results in the formation of a 3D fat crystal network (Pink et al., 2013; Tarabukina et al., 2009).

Fat crystal networks are easily characterized using polarized light microscopy (PLM) in bulk systems (Chen et al., 2002; Tang and Marangoni, 2007). Microscopy is used to better understand food structure and interactions at the molecular level and how they impact macroscopic properties (Aguilera and Stanley, 1999; Flint, 1994; Morris, 2007; Stanley et al., 1998). For fat- and oil-based products, factors such as fat crystal morphology and size distribution of nonfat ingredients are important considerations for product developers (Rousseau, 2007). While this distribution may sometimes be difficult to obtain, sizing by either optical microscopy, gravimetry via sieve stacks, or laser diffraction is possible for objects larger than a few μm.

2.4 Compositional and processing effects

The crystallization pathway is heavily influenced by both composition and processing, e.g., cooling rate (q), $\dot{\gamma}$, etc. (Awua, 2002; Campos et al., 2002; Dhonsi and Stapley, 2006; Hernqvist, 1984; Kellens et al., 2007; Pérez-Martínez et al., 2007). For example, TAG composition can impact polymorphism where larger diversity favors metastable β' crystal formation (Rousseau, 2007). Furthermore, while $\dot{\gamma}$ can complicate polymorphic assignment based on morphology, the rate of crystallization is increased through its ability to facilitate mass transfer and higher ordered polymorphs proliferate (De Graef et al., 2006; Mazzanti et al., 2003; Sato, 2001; Tarabukina et al., 2009). Mass transfer of TAGs during crystal growth is hypothesized to occur either through diffusion, convection, or a combination of the two (Mullin, 1993). The rate of crystal growth (R_c) has been explained by the simple model:

$$R_c = \frac{k(\sigma - 1)}{\eta} \qquad (8)$$

where k is a constant and σ is the degree of supersaturation (Mathlouthi and Genotelle, 1995). Assuming σ is constant, R_c is reduced as η of the system increases.

Large kinetic factors, e.g., large q, favor the formation of many small crystals composed of lower ordered polymorphs according to Ostwald's Step Rule (Bennett et al., 1965; Sato, 2001). DSC has been used to verify this where a small exotherm corresponding to the α polymorph was observed under a larger degree of supercooling (Hartel, 2001). Liquid-state TAGs quickly incorporate within growing crystals under these conditions, resulting in lamellar occlusions and disorganization (Bennett et al., 1965). Transition of these crystals to a higher ordered polymorph may be on the order of months as a result of steric hindrance and large energy barrier (Hartel, 2001; Sato, 1993).

Larger but fewer crystals of higher polymorphic order form under smaller q (Litwinenko et al., 2002; Metin and Hartel, 2005). Furthermore, these conditions minimize thermal gradients (Kleinert, 1961) and allow the complete formation of a lamella before another layer begins (Marangoni, 2005). While this may seem favorable, one potential caveat to a small q is the coexistence of different polymorphs, which may weaken the overall crystal network (Fessas et al., 2005). The effect of q on fat crystallization has been studied further (Baldino et al., 2010).

Cooling endpoint (T_e) is also an important consideration in processing. For example, α crystals form readily in some oils, e.g., PO, at a T_e under 20°C due to the monotropic behavior of TAGs. In addition to β' crystals forming directly from the melt, α crystals simultaneously transition into β' crystals (Fernandes et al., 2013). At T_e values above 20°C, β' crystals form exclusively from the melt (De Graef et al., 2006; Foubert et al., 2006; Litwinenko et al., 2002). A deep understanding of how processing methods may impact fat crystallization is necessary to industry in order to maintain final product quality (Afoakwa et al., 2008c; Altimiras et al., 2007; Debaste et al., 2008; Herrera and Hartel, 2000; Pérez-Martínez et al., 2007).

3. Palm oil in application

Confectionery fats may be split into lauric fats, such as coconut oil and palm kernel oil that are high in lauric acid content, and into nonlauric fats, such as CB, PO, and shea butter. While the handling of lauric fats are quite easy, they are very high in saturated fat content and may not be suitable for some applications, such as confectionery fillings. Furthermore, industry has been continuously seeking nonhydrogenated fats to improve the nutritional profile of their products in response to restricted usage of hydrogenated vegetable oils. PO has quickly risen to the top of fat alternatives in industry due to its natural semi-solid consistency and affordability, however, its physicochemistry is far lesser known than other fats. Here, the production and chemistry of PO is reviewed.

3.1 Production and use

It has been highly recommended to replace saturated fats with poly- and monounsaturated fats in order to control lipoprotein levels (Hruby and Hu, 2016). This is in part due to the association between cardiovascular disease and saturated FAs found in animal-based fats (Neaton and Wentworth, 1992), however, positional distribution of these FAs within TAGs must also be taken into account (Karupaiah and Sundram, 2007). While this
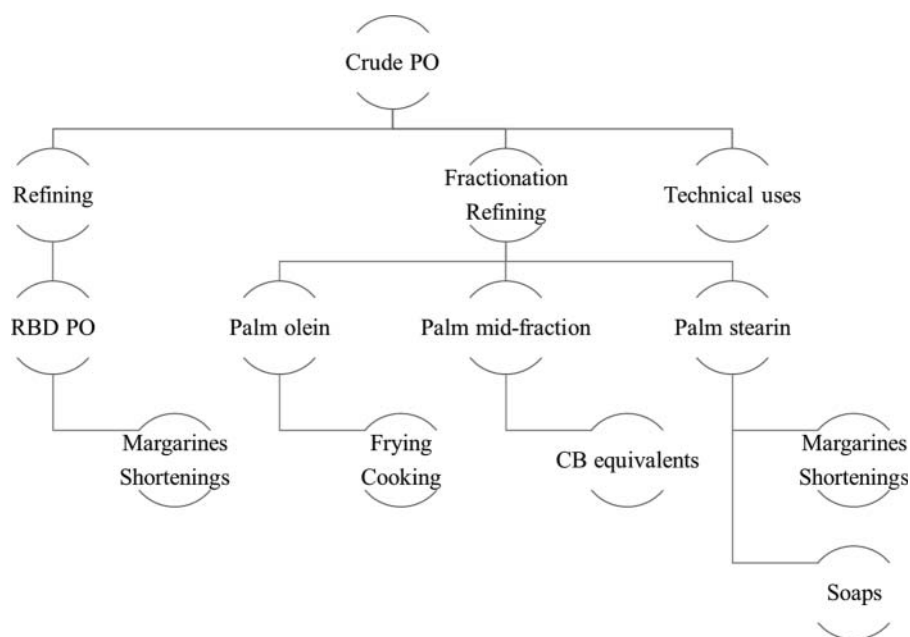
Figure 8. Uses of PO and its fractions (adapted from Basiron, 2001).

generally encourages consumption of plant-based oils, tropical oils are considerably higher in saturation (Edem, 2002; Gee, 2007). This prompted nutritional campaigns in the 1980s which resulted in much of the present-day aversion to PO by consumers (Allen, 2002; Gratzer, 2005; McNamara, 2010).

Malaysia is currently the largest producer and exporter of PO and palm by-products, followed by Indonesia (Sambanthamurthi et al., 2000). It is cheaper to manufacture than any other plant-based oil (Edem, 2002) and has chemical and thermal properties ideal for applications including a natural semi-solid consistency, relatively slow melting properties, and low foaming properties (Cottrell, 1991; Kheiri, 1987; Okiy and Oke, 1984). Uses of PO and its fractions are listed in Fig. 8.

PO is considered a viable substitute for partially hydrogenated oils because of its natural semi-solid consistency and low tendency to become rancid when compared to other plant-based oils (Aftab et al., 2013; Maache-Rezzoug et al., 1998; Sambanthamurthi et al., 2000; Tarrago-Trani et al., 2006). Several commercial products including biscuits, cream fillings, breads and meat patties, have already been successfully formulated with PO and do not contain the *trans* fats that are produced from either partial hydrogenation or high temperature deodorization (Basiron, 2001; Fritsche and Steinhart, 1998; Sherazi et al., 2009). Furthermore, consumption of a palm-based diet was recently shown to reduce low-density lipoprotein levels (Voon et al., 2011). Despite young consumers seeking fat-reduced options when purchasing food (Do et al., 2008), this has traditionally not been an issue with confections since they are typically consumed in small quantities as treats (Rössner, 1997).

3.2 Composition

Palmitic and oleic acid are the main FAs found in ripe drupe of oil palm, at 44% and 39–40%, respectively, followed by linoleic, stearic, and myristic acid (Table 4) (Basiron, 2001; Gee, 2007).

To date, no other plant-based oil is found to be as rich in palmitic acid as palm (Sambanthamurthi et al., 2000).

TAGs account for over 95% of PO content with POP being most abundant (Gee, 2007; Sambanthamurthi et al., 2000). While there exists regioselectivity of unsaturated FAs at the *sn*-2 position, approximately 7–10% of TAGs in PO are trisaturated. Minor components of natural PO include DAGs, MAGs, FFAs, phosphatides, sterols, and trace metals (Sambanthamurthi et al., 2000; Siew and Ng, 1995). The DAG and TAG composition of commercial PO is listed in Table 5 and consists mainly of PPO/POP and OOP/OPO at 27.6 and 22.5%, respectively (West and Rousseau, 2016).

Carotenoids, e.g., β-carotene, aid with vision and are responsible for the dark amber color in raw PO (Edem, 2002). These carotenoids are destroyed after the raw oil has been refined, bleached, and deodorized (Cottrell, 1991). PO is also one of the richest natural sources for tocotrienols (Goh et al., 1985; Sundram and Top, 1994), a subclass of vitamin E that has gained much interest in its role in the circulatory regulation of cholesterol (Sen et al., 2007; Stanley, 2008).

3.3 Processing

Unrefined PO is relatively unstable and must be processed for industrial use (Dian et al., 2006; Kellens et al., 2007). This

Table 4. Typical FA composition of PO (Basiron, 2001).

FA	Composition (%)
Palmitic	44.0
Oleic	39.2
Linoleic	10.1
Stearic	4.5
Myristic	1.1
Linolenic	0.4
Arachidic	0.4
Lauric	0.2

Table 5. DAG and TAG composition of PO (West and Rousseau, 2016).

DAG[*]	Composition (%)	TAG[*]	Composition (%)
1,3-PO	2.0	PPO/POP	27.6
1,2-PO	1.0	OOP/OPO	22.5
1,3-OO	0.8	POL/PLO/OLP	10.1
1,3-PL	0.7	PPL/PLP	7.8
1,3-PP	0.6	PPP	5.5
1,2-OO	0.5	POS/PSO/SPO	5.2
1,2-PP	0.3	OOO	4.4
1,3-SO	0.2	OOS/OSO	2.6
1,2-SO	0.1	LLP/LPL	2.2
1,3-PS	0.1	OOL/OLO	2.1
1,2-PS	0.1	PPS/PSP	1.1
		PLS/PSL/LPS	0.9
		LLO/LOL	0.5
		LLS/LSL	0.3
		AOP/PAO/OPA	0.3
		OOA/OAO	0.2
		LLL	0.1
		LnLP/LnPL/PLnL	0.1
		SSP/SPS	0.1

[*]Palmitic (P); oleic (O); linoleic (L); stearic (S); linolenic (Ln); arachidic (A)

instability comes from the relatively high FFA content of PO, i.e., 5 wt.% (Gee, 2007; Murphy, 2007). The mishandling of natural PO, such as exposure to high temperatures, propagates its acidification, darkening, and uncontrolled enzymatic peroxidation (Chong, 1993; Edem, 2002; Sambanthamurthi et al., 2000). Consumption of these peroxides may lead to health problems including hyperlipidemia, platelet aggregation, and tissue damage (Osim et al., 1992, 1994).

MAGs, FFAs and other minor components are removed from natural PO following initial processing (Gee, 2007; Kellens et al., 2007). The oil may then be fractionated according to its saturation to produce oils that are functionally optimized for specific applications. For example, higher-melting TAGs can be separated from a melt by selective crystallization using a controlled temperature protocol (Hartel, 2001).

Based on temperature-based fractionation, the two main fractions of PO are palm stearin and palm olein (Tshiamala, 2013). Common palm olein melts at 18°C to 20°C and accounts for two-thirds of PO on a weight basis. This liquid fraction is formulated into dressings and cooking oils (Gunstone and Norris, 1983; Stanley, 2008). DAGs co-fractionate into palm olein and produce a eutectic mixture that is responsible for early onset crystallization and clouding (Gee, 2007; Kellens et al., 2007; Siew and Ng, 1996). Palm stearin composes the remainder of PO and melts at 48°C to 50°C. This fraction is often used in margarines and shortenings (Gunstone and Norris, 1983; Stanley, 2008). The higher-melting TAGs in palm stearin are responsible for its higher crystallization rate compared to palm

olein and ability to form β crystals (Che Man et al., 1999). Palm olein and stearin may be further fractionated to produce either mid-fractions used for CB equivalents and other confectionery applications or double-fractionated oils such as super olein, which is used in tocotrienol-rich supplements (Kellens et al., 2007; Stanley, 2008). The physical properties of PO and its fractions are listed in Table 6 (Edem, 2002).

Interesterification is another processing method used to treat PO in order to change its physical properties without changing the FA profile. For example, melting profile, mouthfeel, and spreadability are changed using this technique (Gibon et al., 2007; Kellens et al., 2007). Chemical interesterification completely randomizes the position of FAs along the glycerol skeleton whereas enzymatic interesterification exhibits different degrees of regioselectivity depending on the choice of enzyme (Costales-Rodríguez, et al., 2009). Crossbreeding of the African oil palm with trees naturally lower in saturated content, such as *Elaeis oleifera*, i.e., American oil palm, has also been pursued as a means to generate PO with lower saturated FA content (Sambanthamurthi et al., 2000).

3.4 Recrystallization

PO, in addition to other fats and oils, continues to undergo morphological and spatial re-arrangement during long-term storage as a result of recrystallization. The crystalline phase undergoes orientation and perfection to increase van der Waals interactions and minimize the free energy of the system (Fennema et al., 1973; Hartel, 1998; Metin and Hartel, 2005; Russell et al., 1999; Sonoda et al., 2004). While this is believed to proceed through solid-state transitions, the mechanism is not fully understood and is independent of both temperature and humidity (Fennema et al., 1973; Tshiamala, 2013). It is theorized that recrystallization is driven by either differences in local equilibria of different sized crystals, i.e., Ostwald ripening, the fusion of adjacent crystals, i.e., accretion, or the minimization of crystal surface-to-volume ratios (Hartel, 2001; Kuczynski, 1989).

Recrystallization is of particular concern to the food industry because of its impact on product quality and shelf life. Common examples of recrystallization include the hardening of fondants and "freezer burn" of ice cream (Basso et al., 2010; Hartel, 2001). Palm-based products are particularly prone to recrystallization upon storage. For example, margarine may harden, resulting in a gritty product with poor spreadability due to undesired crystal growth (Omar et al., 2005). The tendency for PO to recrystallize is a result of its DAG content causing slow crystallization rates, although this mechanism is not fully understood. MAGs have been added to PO to aid in nucleation and increase the rate of crystallization (Tshiamala, 2013). They tend to form α crystals which readily undergo α→β' transition (Krog, 2001). While phase diagrams have been used to understand and control crystallization in bulk systems, for complex foods, this is quite complicated (Fennema et al., 1973; Hartel, 2001).

Recrystallization of CB in chocolate, which is responsible for fat bloom, is believed to occur from the growth of pre-existing surface crystals (Jewell, 1972; Timms, 1984; Ziegleder et al.,

Table 6. Physical properties of PO and its fractions (Edem, 2002).

Property	PO	Palm olein	Palm stearin
Melting point (°C)	34.2	21.6	44.5–56.2
Relative density (50°C/water at 25°C)	0.89–0.92	0.91–0.92	0.88–0.89
Refractive index	1.46	1.47	1.45
Moisture and impurities (%)	0.10	0.10	0.00–0.15
Iodine value	47.00–55.83	55.00–61.54	21.60–49.40
Saponification value (mg KOH·g^{-1})	196.0–208.2	189.0–198.0	193.0–206.0
Unsaponifiable matter (%)	0.010–0.500	0.001–0.500	0.100–1.000

1996; Aguilera et al., 2004; Lonchampt and Hartel, 2004; Tietz and Hartel, 2000; Ziegleder and Schwingshandl, 1998). This may be further promoted by a concentration gradient of TAGs (James and Smith, 2009; Lovegren et al., 1976; Sonwai and Rousseau, 2008; Talbot, 1994, 1999). In addition to β_2 crystals, nonfat ingredients further restrict volumetric flow (Q) of liquid-state TAGs by creating a more tortuous path to the surface (Rousseau, 2007). Q is described by Darcy's law:

$$Q = \frac{B * A_c}{\eta} * \frac{\Delta P}{L} \qquad (9)$$

where B is the permeability coefficient, A_c is the cross-sectional area in which flow occurs, ΔP is change in the pressure of the system, and L is the distance in which this pressure change takes place (Dibildox-Alvarado et al., 2004; Marangoni and Wesdorp, 2013).

Using porosimetry (Loisel et al., 1997), well- and over-tempered couverture containing 32 wt. % CB was determined to contain pores at 1 vol.% and 4 vol.%, respectively. These pores are believed to form by contraction upon cooling (Sonwai and Rousseau, 2008). They typically measured 6 μm in diameter by 3 μm in depth according to atomic force microscopy (AFM) with hundreds being randomly distributed within a square centimeter (Rousseau, 2006). It has been theorized that TAGs migrate through these pores by either the aforementioned diffusion equation (Galdámez et al., 2009; Ghosh et al., 2002; Miquel et al., 2001), capillary action (Aguilera et al., 2004; Marty et al., 2005) or pressure-dependent convective flow (Dahlenborg et al., 2015).

In the case of pralines where fillings are made of low-melting oils, e.g., triolein-rich hazelnut gianduja, it is theorized recrystallization occurs via two steps. First, as the shell contracts during storage, liquid-state TAGs migrate from the filling to the surface as cone-like wells (Beckett, 2000). Afterward, these structures grow and harden, serving as hosts for β_1 crystals (Dahlenborg et al., 2011; Smith and Dahlman, 2005; Smith et al., 2007; Sonwai and Rousseau, 2008, 2010). The solubilization between shell and filling TAGs disrupts the phase behavior of the shell and exacerbates recrystallization (Bigalli, 1988; Cebula and Ziegleder, 1993; Couzens and Wille, 1997; Dahlenborg, 2014; Walter and Cornillon, 2002). TAG migration into the shell also lowers its density, causing it to swell, and hardens the filling (Minson, 1990; Ziegleder et al., 1996; Altimiras et al., 2007; Barron, 2007; Miquel and Hall, 2002; Miquel et al., 2001). This swelling effect has previously been explored using confocal chromatic displacement sensors (Svanberg et al., 2012). Additional issues in pralines fillings with high water activity, e.g., water- or alcohol-based, include sugar bloom and mould growth from improper storage (Larumbe et al., 1991; Minifie, 1989).

While it is believed that storage of CB-based confections at 18°C or cooler inhibits solid-state transitions, warmer conditions lead to its rapid onset (Ali et al., 2001; Cebula and Ziegleder, 1993; Lonchampt and Hartel, 2004; Schenk and Peschar, 2004). For example, the recrystallization of well-tempered chocolate into β_1 crystals was observed after 30 days when stored at 30°C (Table 7) (James and Smith, 2009). Storage

Table 7. Effect of temperature cycles on fat bloom formation (Ali et al., 2001).

| | Storage temperature (°C) | | | |
| | 18 | | 30 | |
Week	Fat bloom[a]	Cycles[b]	Fat bloom	Cycles
0	−	7	+	6
1	−	7	++	4
2	−	7	++++	2
3	−	7	++++	1
4	−	7	++++	1
5	−	7	++++	1
6	−	7	++++	1
7	−	7	++++	1
8	−	7	++++	1

[a]−, no bloom; +, weak bloom; ++, bloom; +++, strong bloom; ++++, intensive bloom
[b]one cycle is 30°C (16 h) and 20°C (8 h)

temperature fluctuations may further promote recrystallization (Hachiya et al., 1989), e.g., recrystallization was exacerbated when storage temperatures fluctuated as little as one degree (Hettich, 1966).

MF and its fractions have been shown to inhibit CB recrystallization (Metin, 1997). This was theorized to occur through either slowing down the $\beta_2 \rightarrow \beta_1$ transition by disrupting β_1 lamellar packing (Cook, 1964) or by lowering overall SFC from the eutectic mixture that is formed with CB (Hartel, 1996). Since MF may reduce the SFC via eutectic effects, crystallization rate and crystal size may be reduced as well, potentially softening the product. Higher-melting fractions of MFs may offer a solution to this because they inhibit recrystallization while better preserving SFC (Lohman and Hartel, 1994; Pajin and Jovanovic, 2005). In one study, it was observed that addition of MF at 5.0% and 7.5% reduced the presence of wells, however, sensory properties, e.g., firmness, snap, melting, were just maintained at 5.0% (Sonwai and Rousseau, 2010). MF has been used to prolong the shelf life of confections because of this in addition to its affordability and accordance to the Food and Drug Administration Code of Federal Regulations (Bricknell and Hartel, 1998).

Sugar crystallinity has also been shown to impact fat recrystallization. For example, the appearance of fat bloom was visually reduced formulations with amorphous sugar compared to crystalline powder sugar. This was attributed to amorphous sugar having a smoother surface, and therefore fewer active sites to facilitate recrystallization. Furthermore, its rounded shape may create a more tortuous, closely packed system in comparison to the randomly shaped particulates of powder sugar, which may ultimately hinder oil migration that is responsible for β_1 crystal growth (Bricknell and Hartel, 1998).

Other methods used to study recrystallization have included trained sensory panels (Quevedo et al., 2013), whiteness index (Bricknell and Hartel, 1998; Quevedo et al., 2013), area-scale fractal analysis (Brown et al., 1993), computer vision (Briones and Aguilera, 2005), Raman (Dahlenborg et al., 2012), magnetic resonance imaging (Miquel and Hall, 2002), AFM (Hodge and Rousseau, 2002; Rousseau, 2006), optical profilometry (Rousseau et al., 2010), and scanning electron microscopy (James and Smith, 2009; Wang et al., 2010).

4. Characterization of particle interactions in confectionery products

Fat confectionery texture and crystallization largely depend on the combination of the physical properties of the continuous fat phase, φ, and, importantly, interactions between the ingredients themselves. For example, the particle size distribution and surface area of sugar as well as the emulsifier type and concentration all impact the processability and sensory attributes of fat-continuous products. Similarly, moisture can have a damaging effect as it causes the clustering of nonfat ingredients, resulting in poor mixing. The characterization of particle interactions is thus critical to the establishment of the factors governing the optimized production of confectionery products. To this day, there remains a significant dearth of information in this regard, owing largely to the lack of appropriate research tools. A nascent research avenue in food science is that of force spectroscopy, which offers the unique prospect of determining the extent of particle interactions in confectionery products rich with nonfat ingredients.

4.1 Force spectroscopy

Scientists have romanced the idea of pulling on both sides of a single chemical bond and measuring the force that is required for bond disruption. Such single-molecule experiments have been possible since 1990s using a technique known as force spectroscopy (Noy and Friddle, 2013). While not as developed as its imaging ability, AFM-based force spectroscopy can be used to measure both inter- and intramolecular forces (Han and Serry, 2008; Miles and McMaster, 1995; Morris, 2007). AFM force spectroscopy can yield information such as the conformation and elasticity of proteins (Janshoff et al., 2000), intermolecular interactions in biological and synthetic compounds (Florin et al., 1994; Janshoff et al., 2000; Li et al., 1999; Mate et al., 1987; Merkel et al., 1999; Meyer and Amer, 1988; Noy et al., 1995; Ortiz and Hadziioannou, 1999; Rief, 1997; Wang et al., 2002; Zhang and Zhang, 2003), particulate interactions in colloidal systems (Ducker et al., 1991), localized surface interactions (Frisbie et al., 1994) and ligand-receptor binding affinities (Florin et al., 1994). Recently, it was used to assess the impact of emulsifiers on CB colloidal properties (Middendorf et al., 2015, 2016).

AFM was developed in 1986 (Binnig et al., 1986), which employs a probe that is scanned across a sample where atomic forces between tip and sample are monitored and sample topography can be analyzed (Hodge and Rousseau, 2002; Rousseau, 2007). Cantilever deflection is measured by the "beam bounce" method where a semiconductor diode laser is reflected off the cantilever back and into a position-sensitive split photodiode detector (Fig. 9). The electrical signal that is received by the detector is measured in volts and is proportional to deflection of the cantilever (Cappella and Dietler, 1999).

With AFM-derived force spectroscopy, the tip-sample distance is reduced until "jump-to-contact" has been achieved. Whereas in "contact" mode a feedback loop exists to obtain an image, this is notably absent in force spectroscopy (Han and Serry, 2008). The tip-sample distance is then increased and interactive forces are measured. Tip-sample interactions can be repeatedly measured either at the same surface location or at different locations in
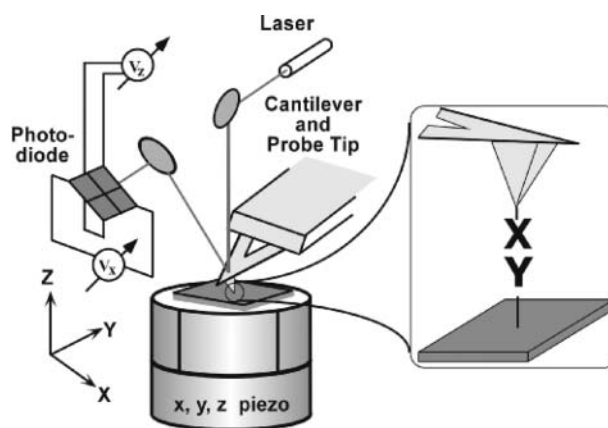

Figure 9. Schematic diagram of AFM (Noy et al., 2008).

order to obtain an interaction map (Owen, 2004). As an alternative to tip retraction, the tip can be intentionally pushed into the sample in a method called nano-indentation (Han and Serry, 2008). Viscoelastic properties typically reserved for rheology, such as Young's modulus, may be obtained. Tip retraction following indentation causes the cantilever to deflect toward the surface because of adhesion (Owen, 2004).

Force spectroscopy is commonly represented as simple curves where the x-axis is the tip-sample distance and y-axis is cantilever deflection measured in either volts or Newtons for raw or calibrated signals, respectively. Information that can be extracted from these plots include hardness, elasticity, and rupture bond length (Fig. 10). These forces may be estimated using the Lennard–Jones potential (V):

$$V = 4\varepsilon\left\{\left(\frac{\sigma}{z_r}\right)^{12} - \left(\frac{\sigma}{z_a}\right)^{6}\right\} \qquad (10)$$

where ε is the depth of the potential well, σ is the distance when force is zero, and z_r and z_a are the distance dependences
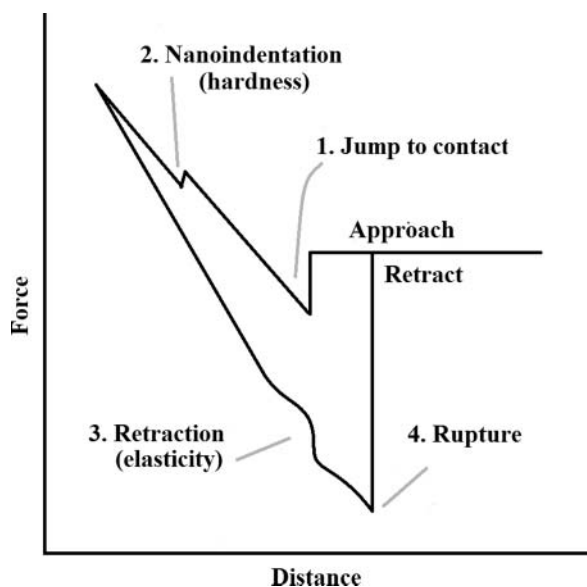

Figure 10. Interpretation of force-distance curves (adapted from Kronenberger, 2006).
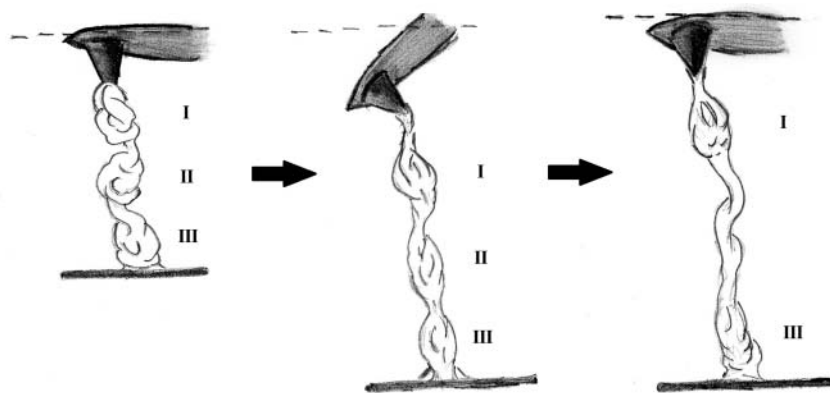
Figure 11. Dimension-dependent conformational analysis of a protein depicting the unfolding of conformation II (adapted from Carrion-Vazquez et al., 1999).

resulting from repulsive and attractive forces, respectively (Seo and Jhe, 2008). In order to calibrate force with the raw voltage that is detected by the PSPD, the spring constant of the cantilever must first be quantified by one of several methods (Han and Serry, 2008). The first method to derive the constant (k) considers the formula:

$$k = 2\pi^3 l^3 w \sqrt{\frac{\rho^3}{E}} f_0^3 \qquad (11)$$

where l is length, w is width, ρ is density, E is Young's modulus, and f_0 is resonance frequency of the cantilever (Han and Serry, 2008). Another method uses a second cantilever with a pre-calibrated spring constant. When this cantilever is pushed against cantilevers of unknown spring constants, these constants can be determined (Hinterdorfer et al., 1996). A third method exposes the cantilever to thermal fluctuations, whereby a thermal noise spectrum is obtained and fitted against a Lorentzian function in order to determine the spring constant (Owen, 2004).

Once the spring constant of the cantilever is known, the deflection distance for a known change in voltage must be determined. This is done by deflecting the cantilever against a clean hard surface. Because of the large force that is exerted on the cantilever, this is often performed post-experiment. After the distance is known, force can be calculated using Hooke's Law:

$$F = kx \qquad (12)$$

where k is spring constant and x is distance determined by the PSPD. Calibration of the cantilever must be performed every time it is mounted to the instrument or between days where conditions such as temperature or humidity differ because deflection may vary. Since deflection values are typically between 0.1 nm to 100 nm, cantilevers with spring constants between 0.01 N·m^{-1} and 1.00 N·m^{-1} are most ideal for force spectroscopy studies (Noy and Friddle, 2013).

4.2 Tip functionalization

The surface of either tip or sample may be intentionally exposed to chemical or biological species in order to study specific molecular–molecular interactions (Han and Serry, 2008; Tang et al., 2008). In sample functionalization, self-assembling monolayers, e.g., silanes on glass surfaces or thiols on gold surfaces, are formed. In tip functionalization, molecules of interest are often adsorbed from solution. Overlaying the interaction-specific force-distance curves with imaging results in chemical or affinity maps—a technique called volume spectroscopy (Han and Serry, 2008; Morris, 2007).

The easiest way to functionalize tips uses short rigid linker molecules followed by spacers, such as alkyl thiols or short-chained polyethylene glycols (PEGs), in order to reduce unwanted tethering. PEGs are often ideal for spacers because of they are both chemically and physically inert and allow tethered molecules to reorient (Ebner et al., 2007). Molecules of interest are diluted with the spacer at 2 mol % upon which the linker is introduced. An issue in AFM force spectroscopy with functionalized tips is distinguishing specific from nonspecific forces with the sample (Noy and Friddle, 2013). Considerations for approaching functionalization in force spectroscopy have been previously reviewed (Blanchette et al., 2008).

Despite little reported on the application of AFM force spectroscopy in food science (Middendorf et al., 2015, 2016), biological topics of interest have included the folding and assembling of macromolecules, construction of biomolecular sensors, and virus-host affinity (Han and Serry, 2008). For example, globular properties exhibit structural anisotropy where the direction of pulling shows unique conformational properties (Fig. 11) (Carrion-Vazquez et al., 2003; Dietz et al., 2006; Gao et al., 2011; Graham and Best, 2011; Jagannathan et al., 2012; Ward and Sweeney, 2012). It is suggested that specific fingerprints of unique unfolding events can be obtained, resulting from secondary and tertiary conformations (Bustamante et al., 2000; Eckel et al., 2003; Rief, 1997). In another study, graphite demonstrated different stabilities when pulled either parallel or perpendicular to its polycyclic rings (Zheng et al., 2013). Measurements of polysaccharide chains were also studied using force spectroscopy (Rief et al., 1997; Zhang and Marszalek, 2006).

5. Conclusions

The quality of fat-based confections is not only derived from the physical properties of the continuous fat phase, but also its chemistry with the nonfat ingredients contained within. The amount of fat affects the wetting of nonfat ingredients, behaving as a lubricant and maintaining proper fluidity, while the nonfat ingredients provide surfaces off of which fat can nucleate but may also change viscosity and mobility of the species that contribute to crystal growth. The way in which these ingredients interact strongly influences the path of fat crystallization and ultimately perception of the product by the consumer. Hardness and spreadability are just two such properties that depend heavily on this relationship. An understanding of ingredient interactions is viable to the success of any product and has become particularly important in confectionery applications, particularly those that are palm-based, where quality is largely determined through trial and error. This opens the door to untapped venues of food science, such as force spectroscopy, where specific ingredient-ingredient interactions can be characterized and used to better predict how such systems will crystallize.

Acknowledgments

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