



Effect of additives on isothermal crystallization kinetics and physical characteristics of coconut oil

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ABSTRACT

The effect of lauric acid and low-HLB sucrose esters (L-195, S170) on the isothermal crystallization of coconut oil was investigated by differential scanning calorimetry. The fundamental crystallization parameters, such as induction time of nucleation and crystallization rate, were obtained by using the Gompertz equation. The Gibbs free energy of nucleation was calculated via the Fisher–Turnbull equation based on the equilibrium melting temperature. All additives, investigated in this work, proved to have an inhibition effect on nucleation and crystallization kinetics of coconut oil. Our results revealed that the inhibition effect is related to the dissimilarity of the molecular characteristics between coconut oil and the additives. The equilibrium melting temperature (T_m^0) of the coconut oil–additive mixtures estimated by the Hoffman–Weeks method was decreased with the addition of lauric acid and increased by using sucrose esters as additives. Micrographs showing simultaneous crystallization of coconut oil and lauric acid indicated that strong molecular interaction led to the increase in lamellar thickness resulting in the T_m^0 depression of coconut oil. The addition of L-195 modified the crystal morphology of coconut oil into large, dense, non-porous crystals without altering the polymorphic occurrence of coconut oil. The enhancement in lamellar thickness and crystal perfection supported the T_m^0 elevation of coconut oil.

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1. Introduction

Crystallization studies of fat systems are of great scientific and practical importance, since a proper understanding of fat crystallization kinetics is essential to control industrial operations which provide final products possessing desired characteristics. Furthermore, comprehensive studies focusing on the influence of crystallization parameters and formulation of fats (composition and additives) are especially needed in the melt fractionation technology. However, the crystallization kinetics of fats has not been well clarified so far and only few quantitative kinetic data are available which are based on empirical observations (Foubert et al., 2003). This is due to the fact that natural fats are regarded multi-component mixtures containing a big diversity of triglycerides (TAGs) which results in a broad melting temperature range and a complex crystallization behavior (Liang et al., 2003).

The crystallization conditions have strong influence on the thermal characteristics of crystalline products (Kellens et al., 1990). In general, crystallization involves 2 kinetic steps. Firstly, nucleation can be referred to the birth of crystals. In order to initiate the nucleation, supercooling or supersaturation must be applied

as a thermodynamic driving force (Garside, 1987). Once the nuclei are formed, they grow and develop into crystals. In fact, nucleation and crystal growth always occur simultaneously (Boistelle, 1988). According to Ulrich, nucleation has the strongest predetermining influence on product properties, such as purity of the crystalline product, solid fat content, crystal habit or crystal size and size distribution (Ulrich and Strege, 2002).

In order to perform kinetic studies of fat crystallization, the experimental technique must be sufficiently sensitive to detect nucleation and discard crystal growth (Cerdeira et al., 2004). The common techniques, which are frequently used in modeling studies by monitoring the isothermal crystallization behavior of fats as a function of time, are differential scanning calorimetry (DSC) (Kellens et al., 1990; Toro-Vazquez et al., 2000; Vanhoutte et al., 2002), nuclear magnetic resonance spectroscopy (NMR) (Ng and Oh, 1994; Kloek et al., 2000; Wright et al., 2000) and turbidimetry (Herrera et al., 1999; Toro-Vazquez et al., 2002; Cerdeira et al., 2003). These techniques differ in their theoretical background, advantages and disadvantages depending on the fat systems and the experimental conditions.

The crystallization kinetics is evaluated by fitting mathematical models to the experimental data and the important parameters connected to nucleation and crystallization kinetics are extracted. So far, a considerable number of models have been used to characterize the isothermal crystallization kinetics of fats, e.g. the Gompertz (Kloek et al., 2000; Vanhoutte et al., 2002) and the

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Foubert model (Foubert et al., 2002; Foubert et al., 2003) or the most commonly used Avrami model (Herrera et al., 1999; Foubert et al., 2002). The Gompertz model has been reported to show better fit to the multiple crystallization peaks of fats than the model developed by Avrami (Kloek et al., 2000; Vanhoutte et al., 2002), while the Avrami model is meant to fit only a single crystallization peak (MacNaughtan et al., 2006). The Foubert model is relatively newly developed and contains kinetic parameters with; however, unclear explanations.

In this study, coconut oil was chosen as a model substance for a fat crystallization kinetic study. It is one of the most commonly used oils in several applications, e.g. food products (Rossell, 1985), cosmetics, pharmaceutical preparations and biodiesel (Abigor et al., 2000), in which crystallization is always essentially involved. Compared to other fats, the composition and the phase behavior of coconut oil are relatively simple containing approximately 90% saturated fatty acids and half of them are lauric acid (Canapi et al., 2005; Marina et al., 2009), which makes it a suitable model for kinetic studies (Timms, 1984). In addition, TAGs of coconut oil consist of more than 15% of C6–C10 fatty acids which belong to a medium-chain fatty acid group (MCFAs) promoting human health and reducing the risk of atherogenic or heart diseases (Beermann et al., 2003).

In spite of its favorable properties and its frequent industrial application, concrete information in the kinetic study of coconut oil crystallization has rarely been published. The effect of minor components on the crystallization kinetics of coconut oil was quantified by using the Arrhenius equation previously, where the effect of supercooling was excluded (Gordon and Rahman, 1991). The present work provides a contribution to the understanding of isothermal crystallization behavior and crystal morphology of coconut oil affected by additives by using the Gompertz model. The experiments concerning thermal behavior and crystallization kinetics were performed by DSC.

2. Materials and methods

2.1. Sample preparation

Refined, bleached and deodorized (RBD) coconut oil (Ostthüringer Nahrungsmittelwerk Gera GmbH, Gera, Germany) was used as a model substance. Lauric acid (98% purity, Sigma–Aldrich Company, Germany), Ryoto-sucrose laurate (L-195) and Ryoto-sucrose stearate (S-170) (Syntapharm Ges. F. Pharmachemie mbH, Germany) were utilized as additives. The samples were prepared by melting the mixture of coconut oil and the additives (15%, w/w lauric acid, 1%, w/w sucrose laurate and 1%, w/w sucrose stearate) at 80 °C for 30 min. The same batch of all substances was used throughout the experiments.

2.2. Thermal analysis

Thermal behavior of fats is usually studied by DSC (Lopez and Ollivon, 2009). Thermal analysis was performed by using a differential scanning calorimeter (Mettler Toledo 12E, Giessen, Germany). The temperature and heat of fusion were calibrated with indium and lead (onset temperature 156.6 and 327.5 °C, respectively). Approximately 5.5 mg of each mixture were weighted and sealed in an aluminum pan. An empty pan was used as reference throughout the experiments.

2.2.1. Thermal profile analysis

The sample was held at 80 °C for 10 min to destroy its crystal memories, then cooled to –10 °C at a rate of 2 K/min and held for 3 min at this temperature. It was then again heated from –10 to

80 °C at the same rate. The melting profile of the samples was taken from the reheating cycle.

2.2.2. Isothermal crystallization analysis

The sample of each mixture underwent the isothermal run by holding it at 80 °C for 10 min to destroy crystal memories. The melts were then rapidly cooled down to the crystallization temperature at a cooling rate of 10 K/min and isothermally held at this temperature for 30 min to observe the crystallization process. Afterwards, the melting thermogram was recorded by heating the sample at a rate of 2 K/min. The isothermal crystallization exothermic was taken for the kinetic modeling. Samples were reused for further experiments by repeating the same procedure before cooling again to the next isothermal temperature. Considering the fact that saturated fats are relatively unreactive and the continuous reheating of the samples have only little influence on their thermal behavior (MacNaughtan et al., 2006), the results related to a specific concentration were obtained by using the same sample. Our preliminary results also showed that the repetition of the experiment resulted in the same kinetic data.

2.3. Crystallization kinetics

The exothermic peak was taken from the isothermal crystallization step to characterize the crystallization kinetics of coconut oil by using the modified Gompertz equation (Eq. (1)). This model was originally used to predict bacterial growth (Zwietering et al., 1990). However, it was claimed that there were several kinetic similarities between the crystallization of fats and bacterial growth. The production of bacteria was comparable with the nucleation and growth of crystals and the consumption of nutrients were referred to the decrease of supersaturation (Kloek et al., 2000). The derivation from the original Gompertz equation to the reparameterized version was explained elsewhere (Foubert et al., 2003).

$$F(t) = Ae^{-e^{(\mu e^{(\tau-t)/A})+1}}, \quad (1)$$

where $F(t)$ is the relative percent of solid fraction crystallized at time t , A is the maximum fraction of solid fat in percent, μ is the maximum increase rate in crystallization (tangent to the inflection point of the crystallization curve) and τ is the induction time (intercept of the tangent at the inflection point with the time-axis). The value of $F(t)$ was calculated by integrating the isothermal crystallization peak according to Eq. (2):

$$F(t) = \frac{\Delta H_t}{\Delta H_{total}} \times 100, \quad (2)$$

where ΔH_t is the partial area under the DSC crystallization peak at time t and ΔH_{total} is the total area under the crystallization curve. The cumulative solid fraction is plotted against time. The induction time of nucleation and the maximum crystallization growth rate can be obtained by fitting the Gompertz model to the experimental data.

The induction time of nucleation (τ) is generally taken as the reverse proportion of the nucleation rate (J) which can be used to calculate the activation energy of nucleation. This energy, which represents the energy barrier that the molecule has to overcome in order to develop a stable nucleus, can be evaluated by using the Fisher–Turnbull equation (Eq. (3)) (Ng, 1990). The Gibb's free energy calculated from this equation is associated with the degree of supercooling and molecular diffusion. Although, this equation was originally derived for a single component (Turnbull and Fisher, 1949), it is applicable in multi-component systems of vegetable oils and milk fats (Ng, 1990; Toro-Vazquez et al., 2000; Chen et al., 2002;

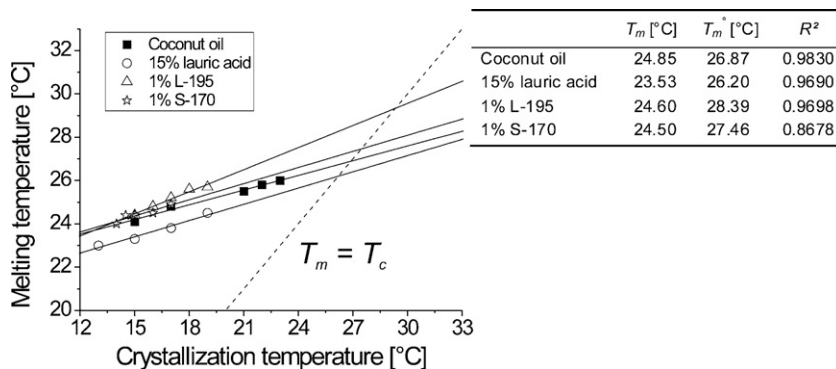


Fig. 1. Determination of equilibrium melting temperature according to the Hoffman–Weeks method (T_m : melting point obtained from the experiments; T_m° : equilibrium melting temperature).

MacNaughtan et al., 2006).

$$J = \left(\frac{NkT}{h}\right) e^{(-\Delta G_d/kT)} e^{(-\Delta G_c/kT)}, \quad (3)$$

where J is the nucleation rate, N is the Avogadro number, k is the gas constant per molecule, h is the Planck constant and T is the temperature. ΔG_d is the Gibb's free energy of volume diffusion. For spherical nuclei, ΔG_c is Gibb's free energy of nucleation which is related to the surface-free energy of the crystal-melt interface (σ) and the degree of effective supercooling (ΔT) (Eq. (4)):

$$\Delta G_c = \left(\frac{16}{3}\right) \frac{\pi\sigma^3(T_m^\circ)^2}{(\Delta H)^2(\Delta T)^2}, \quad (4)$$

where ΔH is the heat of fusion. The effective supercooling (ΔT), which is defined as the difference of the equilibrium melting temperature (T_m°) and the crystallization temperature (T_c), is the driving force of crystallization. The equilibrium melting temperature has been widely used for the characterization of polymers which are also regarded as multi-component systems (Hiromi, 1993). It is the thermodynamic quantity defining the melting temperature of an equilibrium crystal with an infinite size. The direct measurement of T_m° is not possible. It can only be determined by extrapolation since polymers never reach a completely crystalline state (Al-Hussein and Strobl, 2002). The value of T_m° can be determined from the intersection of the so-called equilibrium line ($T_m = T_c$) and the apparent melting point (T_m) of the mixtures by using a remelting thermogram recorded after an isothermal crystallization cycle (Hoffman and Weeks, 1962). This method was introduced for fat systems (Toro-Vazquez et al., 2000) since there are several analogies between fats and polymer molecules. Generally, the experimentally determined melting point of fats can be assumed as the melting point considering the fact that fats are crystalline substances and do not undergo glass transition (Cerdeira et al., 2004). However, in the fat system containing additives such as sucrose esters, the effect of partial recrystallization and the partly amorphous structure have to be taken into account (Szűts et al., 2007). As a result, to perform kinetic study of such a system, the determination of equilibrium melting temperature is essential.

The main barrier to diffusion in TAGs system is proportional to the probability that a triglyceride molecule at the crystal surface is in the right conformation for the incorporation into the nucleus. Therefore, the diffusion term (ΔG_d) from Eq. (3) can be replaced by $\alpha\Delta S/k$ where α is a fraction of molecules that should be in the right conformation for incorporation in a nucleus, ΔS is a decrease of entropy on crystallization of 1 mol TAGs ($\Delta S = \Delta H/T$) (Kloek et al., 2000). Eq. (3) can be rewritten as follows:

$$\tau^{-1} = J = \left(\frac{NkT}{h}\right) e^{(-\alpha(\Delta S/k))} e^{(-16/3)(\pi\sigma^3(T_m^\circ)^2/(\Delta H)^2kT(\Delta T)^2)} \quad (5)$$

After mathematical rearranging and applying natural logarithm, the relation of induction time and temperature can be deduced as shown in Eq. (6):

$$\ln \tau T = \ln \frac{h}{Nk} + \alpha \frac{\Delta S}{k} + \left(\frac{16}{3}\right) \frac{\pi\sigma^3(T_m^\circ)^2}{(\Delta H)^2kT(\Delta T)^2} \quad (6)$$

According to Eq. (6), the linear regression with a positive slope (s) can be obtained from the plot between $\ln \tau T$ and $1/T(\Delta T)^2$. The Gibb's free energy of nucleation is then calculated based on the slope by utilizing Eq. (7).

$$\Delta G_c = \frac{sk}{\Delta T^2} \quad (7)$$

2.4. Crystal morphology of coconut oil

Approx. 3 mL of the fat samples was filled into a microscope cell (diameter 3.6 cm) equipped with a programmable thermostat. The temperature of the sample was set to 50 °C constantly for 15 min. Afterwards, the sample was cooled to the crystallization temperature with the cooling rate of 1 °C/min. When the crystallization temperature has been reached, the fat sample was kept isothermally. The crystal morphology of the sample after 60 min isothermal crystallization was visualized by a light microscope (magnification 3.3 × 5, Olympus BH2-UMA, Olympus Optical Co., Ltd., Tokyo, Japan).

3. Results and discussion

3.1. Equilibrium melting temperature

Equilibrium melting temperature of the fat mixtures evaluated according to the Hoffman–Weeks method (Fig. 1) shows a good linearity of the data plots ($R^2 > 0.85$).

In this work, the equilibrium melting temperature (T_m°) of the fat mixtures is always higher than the melting point obtained from the experiments (T_m). This can be explained by the fact that T_m° is based on the calculation referring to perfect crystalline state, while T_m is related to the formed crystals under the applied experimental conditions.

The addition of lauric acid led to the equilibrium melting point depression of coconut oil. This indicates miscible mixtures exhibiting significant intermolecular interactions between coconut oil and lauric acid (Runt et al., 1984). In contrast, the equilibrium melting point elevation of coconut oil was observed with the addition of both sucrose esters. The increase in T_m° might be explained by the enhancement of lamellar thickness and crystal perfection related to the addition of sucrose esters. In addition, the as-formed crystals may thicken and reorganize into a higher melting form during

Table 1

Kinetic parameters quantified by the Gompertz and Fisher–Turnbull equations.

Fat mixtures	A^a [%]	μ^a [%/min]	τ^a [min]	ΔG_c^a [kJ mol ⁻¹]	R^2 Gompertz ^a	R^2 Fisher ^a
Coconut oil	100.36	55.35	3.55	1.48	0.9987	0.8925
15% lauric acid	99.79	18.29	7.29	3.31	0.9990	0.9973
1% L-195	105.65	12.11	6.18	4.93	0.9991	0.9861
1% S-170	105.62	11.85	12.06	13.68	0.9952	0.8530

^a Abbreviations— A : the maximum fraction of solid fat; μ : the crystallization rate; τ : the induction time of nucleation; ΔG_c : the Gibb's free energy of nucleation; R^2 : the correlation coefficient.

thermal analysis (Rim and Runt, 1983) and lead to the increase in T_m of the mixtures.

3.2. Isothermal crystallization kinetics

Fig. 2 shows the kinetic model fittings to the crystallization data of coconut oil mixtures in the presence of additives. The correlation coefficient of the plot indicates that the Gompertz model fits perfectly to the crystallization data of these fat mixtures (Fig. 2A). A fairly good linearity of the plot of the Fisher–Turnbull equation revealed that the nucleation kinetics of the fat systems containing additives can be characterized by the Fisher–Turnbull equation (Fig. 2B). The kinetic parameters and the correlation coefficient of the kinetic model fittings were summarized in Table 1.

As summarized in Table 1, the induction time of nucleation increased with the addition of lauric acid and low-HLB sucrose esters. This is in agreement with previous studies (Gordon and Rahman, 1991; Martini et al., 2004), which revealed that the addition of additives increased ΔG_c of coconut oil. The larger value of Gibb's energy implies that the nucleation is slower in a system containing additives compared to a pure melt. This allows the conclusion that all additives have inhibition effects on the nucleation

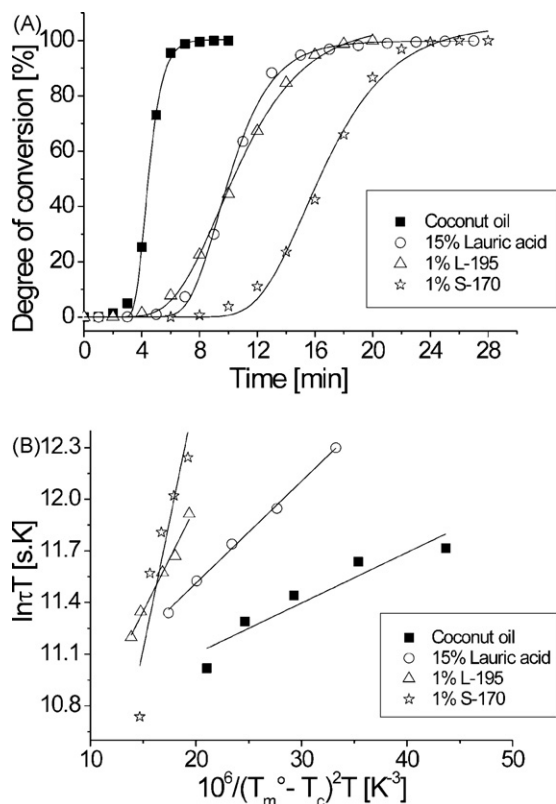


Fig. 2. Model fittings of the crystallization data. (A) Gompertz model fitted to the crystallization data of coconut oil mixtures at a crystallization temperature of 14 °C; (B) Fisher–Turnbull model fitted to the nucleation data of the same fat systems.

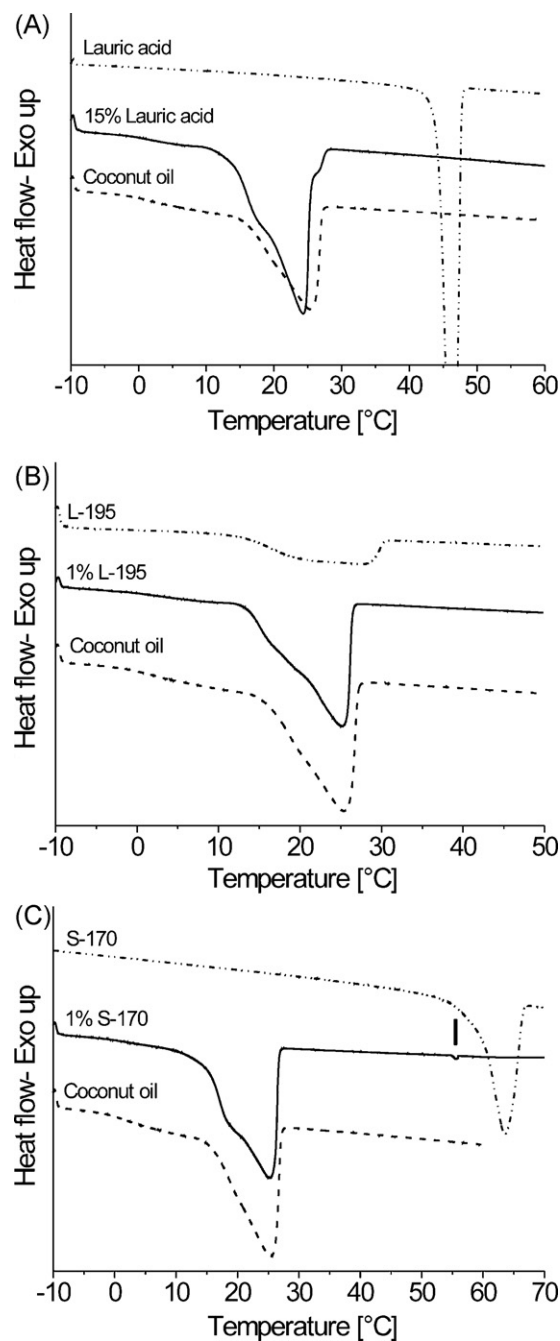


Fig. 3. Melting profiles of coconut oil systems (A) pure coconut oil, coconut oil + 15% lauric acid and pure lauric acid, (B) pure coconut oil, coconut oil + 1% L-195 and pure L-195 and (C) pure coconut oil, 1% S-170 and pure S-170.

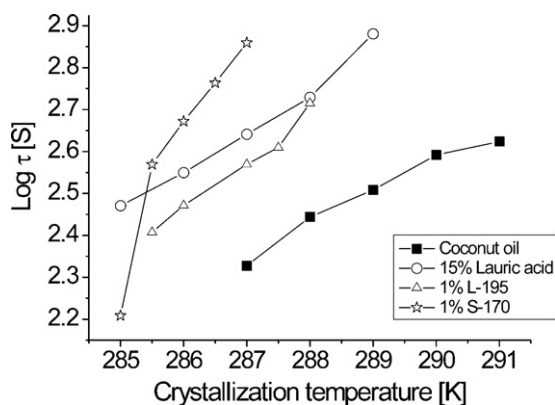


Fig. 4. Nucleation curves of coconut oil mixtures.

of coconut oil. Lauric acid and L-195 have a less pronounced inhibition effects compared to S-170 that shows the strongest impact on the nucleation kinetics. This effect could be related to the dissimilarity in the molecular shape of the additives and the triglycerides of coconut oil. Since lauric acid is the main fatty-acid component of coconut oil, it has higher possibilities to integrate into the nucleus due to the similar molecular structure (Gordon and Rahman, 1991). However, there are greater differences in the molecular structure between sucrose esters and coconut oil compared to fatty acids. Hence, the dissimilar part of the additives can interfere the nucleation process resulting in a more pronounced inhibition effect (Hartel, 2001)

It must be noted that the Gibb's free energy of nucleation calculated in this work is significantly lower than those published in a previous work of Gordon and Rahman (1991). This can be explained by the shortcoming of the Arrhenius model that does not include the degree of supercooling as stated in the introduction and resulting in higher values. The values of Gibb's free energy calculated in

this work are in the similar range as reported by other papers (Ng, 1990; Toro-Vazquez et al., 2002).

The maximum crystallization rate (μ) which was quantified by the Gompertz model is the kinetic parameter showing a reverse tendency to the induction time (τ) calculated via the Fisher–Turnbull equation. This is due to the crystallization rate being dependent on the number of nuclei available for crystal growth. It is remarkable that even though these sucrose esters have quite the same value of crystallization rate, the Gibb's free energy of sucrose laurate is considerably lower than that of sucrose stearate. This indicates that the retardation of coconut oil crystallization with the addition of sucrose ester is related to the nucleation step and can be attributed to the sucrose ester itself.

3.3. Melting behavior of coconut oil mixtures

Fig. 3 depicts the melting profiles of coconut oil in presence of additives. The melting curve of coconut oil is relatively simple with one major endotherm and a small shoulder on the lower temperature side. The melting curve for the mixture of coconut oil and lauric acid (Fig. 3A) exhibits the major peak of coconut oil which is slightly shifted to lower temperatures. The endotherm of lauric acid is also shifted from its original position and overlaps the major peak of coconut oil resulting in distinctive shoulder (I) on the right side. The similar behavior was found for the mixture of coconut oil and S-170 (Fig. 3C). However, the distance between the shifted and the original melting peak position or so-called melting drop of the S-170 peak is smaller than that of lauric acid (melting drop approx. 10 and 20 °C in the system of S-170 and lauric acid, respectively). A larger melting drop indicates a stronger interaction and dilution when mixing coconut oil with lauric acid in comparison to sucrose esters and some interdiffusion or cocrystallization resulting in mixed crystals. This behavior was suggested to strongly depend on the similarity in molecular characteristics between low and high melting components (coconut oil is regarded as low while additives

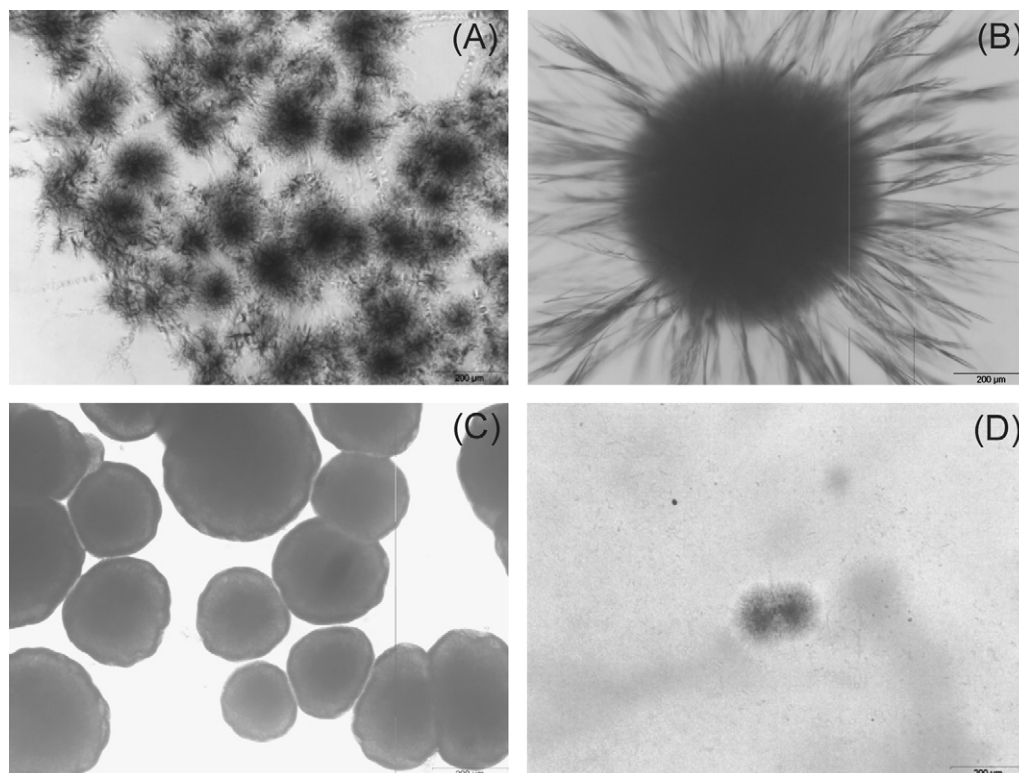


Fig. 5. Crystal morphology of pure coconut oil (A), coconut oil in the presence of 15% lauric acid (B), 1% L-195 (C) and 1% S-170.

as high melting component). This information is in good agreement with the kinetic results and supports the hypothesis in equilibrium melting temperature depression with lauric adduct. However, the peak of L-195 (Fig. 3B) cannot be detected. It is probably due to the overlapping of the L-195 peak in the major peak since L-195 has similar melting range like coconut oil.

3.4. Polymorphic occurrence of coconut oil mixtures

The polymorphism of TAGs refers to the ability of molecules to arrange themselves in a crystal lattice in a number of different packing forms. The plot of log induction time as a function of crystallization temperature or so-called the nucleation curve could be used to predict the polymorphic occurrence of palm oil and its derivatives (Ng, 1990; Chen et al., 2002). In this work, the nucleation curve was applied to predict the effect of additives on the polymorphic occurrence of coconut oil.

Fig. 4 shows a continuous nucleation curve of coconut oil without a jump of the induction time. This behavior can be interpreted that one polymorph crystallized in the applied temperature range. This is in agreement with a previous report that coconut oil has one stable polymorphic form called β' -2 (Timms, 1984).

The nucleation behavior of the coconut oil – additive mixtures is similar to that of coconut oil showing continuous curves. However, the nucleation curves of coconut oil in the presence of additives are shifted toward the lower temperature range. This reveals that the nucleation of coconut oil in the presence of additives is always slower at every temperature since the nuclei need more time to initiate the nucleation. This result implies that even though, the thermodynamics and kinetics of coconut oil crystallization were altered by these additives, the additives have no influence on the polymorphic occurrence of the coconut oil.

3.5. Crystal morphology of coconut oil mixtures

The crystal habits of coconut oil in the presence of additives are demonstrated in Fig. 5. The native crystal morphology of coconut oil is a spherulite consisting of needle crystals (Fig. 5A). The concentration of additives was reported to affect the morphological characteristics and the final microstructures of the crystals (Shi et al., 2005). The spherical crystals were still observed in the mixture of coconut oil and 15% lauric acid showing the existence of mixed crystals of spherical crystals surrounded by needle-like ones (Fig. 5B). The formation of these crystals was explained in the previous study (Chaleepa et al., 2010) indicating the strong interaction between coconut oil and lauric acid. The addition of L-195 led to the modification of coconut oil crystal morphology (Fig. 5C). The round, non-porous crystals are formed at a concentration of 1% L-195. In addition, the crystal size is significantly larger than pure coconut oil. This result is in accordance with the increase of the equilibrium melting temperature of the coconut oil with the addition of L-195 since the lamellar thickness, crystal size and crystal perfection (shape) of the coconut oil can be enhanced. When coconut oil was crystallized with the addition of 1% S-170, the obtained crystals were smaller (Fig. 5D). However, the morphology was still the same as of the pure melt. On the basis of this, it can be assumed that the addition of S-170 has an influence on the crystallization kinetics but not on the morphology and polymorphism of coconut oil crystals.

4. Conclusion

Summarizing the results, it can be concluded that the Gompertz model and the Fisher–Turnbull equation can be successfully utilized to characterize the isothermal crystallization kinetics of fats in the presence of additives, using coconut oil as a model

substance. The information on equilibrium melting temperature and nucleation kinetics in the terms of Gibb's energy and polymorphic occurrence of the fat mixtures were obtained via the Hoffman–Weeks methods and Fisher–Turnbull equation.

The application of additives can either increase or decrease T_m° of coconut oil. In general, the reduction of T_m° is found in the miscible system having strong interaction between the fat and the additive. However, the addition of L-195 increased the T_m° of coconut oil significantly indicating an enhancement in crystal size, lamellar thickness and crystal perfection. This hypothesis was supported by the micrographs of the crystals.

All additives types applied in this study, especially sucrose esters, had an inhibition effect on the crystallization kinetics of coconut oil. This effect strongly depends on the dissimilarity in molecule shape. The greater the difference in molecular structure between the additives and fats is, the more pronounced is the inhibition effect. The additives did not alter the polymorphic occurrence of coconut oil, even though the crystal morphology of the coconut oil was modified into round, non-porous crystals by the addition of L-195. However, the applied mathematical approach can be regarded only as a predicting tool of polymorphism and an experimental verification is needed to confirm the polymorphic occurrence e.g. by X-ray diffraction.

On the basis of the results, it is necessary to evaluate the effect of these additives on the functional properties of coconut oil such as solid fat content, shear viscosity and texture. Further experiments with the sucrose laurate containing higher HLB values are of interest in order to provide more information on the mechanism of crystal morphology alteration.

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