

Research Article

Isothermal Crystallization Kinetics of Palm Oil with Additives

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Abstract: This study investigates the isothermal crystallization kinetics of palm oil with additives by Differential Scanning Calorimetry (DSC). The induction time of nucleation and crystallization are obtained by simulating the crystal process using the Gompertz model. The equilibrium melting temperature is obtained via the Hoffman-Weeks methods. The Gibbs free energy of nucleation was calculated by using the Fisher-Turnbull equation and the equilibrium melting temperature. The results indicate that the span 85 has an inhibition effect on nucleation and crystallization kinetics of palm oil. The span 85 can raise the equilibrium melting temperature of palm oil. The span 85 can obviously delay the induction time of nucleation and crystallization at 0.01 and 0.1% level. Although span 85 at 0.05% concentration level also can delay the induction time, it exhibits an effect of promoting nucleation. However, the crystal is uncomplicated in the system containing additives compared to the pure palm oil.

Keywords: Crystallization kinetics, fisher-turnbull, Gompertz, palm oil, span 85

INTRODUCTION

Palm oil is one of important oils in the world oils market. It is widely used in food industry for its good oxidative stability and relative low price. But it is well known that 24°C palm oil presents a liquid state at room temperature, when the temperature dropped to 20°C, clear palm oil will become turbid and as time becomes longer, the phenomenon of the solid-liquid separation and surface skinning will occur. So the cyclic heating is required in the following storage, transportation and processing. This will lead to oxidative rancidity of palm oil and energy consumption. Therefore, it has important scientific and social significance to find a food additive to improve product weather-ability.

In recent years, studies about the effects of additives on the crystallization behavior of palm oil have become a hot. Siew and Ng (1999) pointed out that the pure palmitic acid diacylglycerol (2.5~10%, w/w) hinder the nucleation and crystallization process of palm oil triglycerides. Saberi *et al.* (2011) studied the crystallization kinetics of palm oil mixed with palm-based diacylglycerol (2~50%, w/w) and pointed out that when the addition amount of 5% can reduce the rate of nucleation. Toro-Vazquez *et al.* (2000) studied the crystallization kinetics of palm stearin in blends with sesame seed oil and pointed that the crystallization behavior of palm stearin in sesame oil is mainly associated with the crystallization of tripalmitin and crystallization in the β_1 state in the 80% mixture system required more free energy for nucleation than β_1'

crystallization in the 26, 42 and 60%, respectively mixture systems. Although there are a lot of information about the research of the crystallization behavior of palm oil, most studied are based on the solid crystal structure and the evolution and the use of additives is larger.

Span 85 additives used herein can effectively prevent crystallization of palm oil and the studies of dynamics of delaying the nucleation have not been reported. This study used the Gompertz model (Kloek *et al.*, 2000; Vanhoutte *et al.*, 2002) to simulate the entire crystallization and the molecular aggregation structure of fats and measured by Differential Scanning Calorimetry (DSC) (Toro-Vazquez *et al.*, 2000; Vanhoutte *et al.*, 2002) to obtain the exact experimental data and kinetic parameters.

MATERIALS AND METHODS

Sample preparation: Amount of 24°C refined palm oil samples and sorbitan trioleate (span 85, food grade, Shanghai Chemical Reagent Company) additives were weighed accurately. (0.01, 0.05 and 0.1%, respectively w/w) span 85 was mixed with the pure palm oil respectively as samples. The samples were added to a reaction flash equipped with a stirrer and heated in a water to melt at 80°C for 30 min.

Dynamic thermal analysis: DSC analysis of the samples was performed with a U.S. TA Instrument Q100 DSC. The temperature and heat of fusion were

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calibrated with indium and lead. The sample (completely melted at 80°C before) 6~8 mg was weighed into an aluminum pan. The sample was heated to 80°C in the DSC and maintained at that temperature for 10 min to destroy its crystal memories, then cooled to -10°C at a rate of 3°C/min and held for 10 min at this temperature. It was then again heated from -10 to 80°C at the same rate. Each sample is analyzed repeatedly. The melting temperature of the sample was taken according to the endothermic and exothermic process.

Isothermal crystallization analysis: The sample of each mixture underwent the isothermal crystallization by the U.S. TA Instrument Q100 DSC. The sample was heated to 80°C for 30 min to destroy crystal memories initially, then the melts were cooled to a presupposed crystallization Temperature (Tc) at a rate of 10°C/min and keep the Tc until heat of the heat and time diagram is no longer change. Afterward, the sample was heated at a rate of 1°C/min to record the melting thermogram which was used to study the kinetic model of the melting process. Samples were reused for further experiments by repeating the same procedure before cooling to the next isothermal temperature. Considering the fact that palm oil is relative chemical stability and continuous reheating of samples have only little influence on their thermodynamics property (MacNaughten *et al.*, 2006), so the results related to a specific concentration were obtained for using the same sample.

Kinetic analysis: As the crystallization process of samples is more complex, data from isothermal crystallization does not conform to the first law of thermodynamics. According to preliminary results and data, the experimental value of the isothermal crystallization was simulated to characterize the crystallization kinetics of the palm oil with the help of the improved Gompertz equation (Foubert *et al.*, 2003) Eq. (1):

$$C(t) = C_0 \exp[-e^{((v(\tau-t)/C_0)+1)}] \quad (1)$$

In the Eq. (1), C (t) is the relative percentage of solid components of the crystallization, C₀ is the maximum percentage of the crystalline solid, v is the maximum growth rate during the crystallization and τ is the induction time. C (t) could be obtained by the relative percentage of absorbance detected at different time, calculated according to Eq. (2):

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

In Eq. (2), 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 induction time of nucleation (τ) and the maximum growth rate (v) can be obtained by fitting Gompertz model to the experimental data and using the nonlinear least-squares curve with Microsoft EXCEL Solver.

The activation energy of nucleation can be evaluated by using the Fisher-Turnbull equation (Ng, 1990) Eq. (3). The Gibbs free energy is related to super-cooling degree and molecular diffusion. This equation is applicable in multi-component systems of vegetable oils and milk fats (Toro-Vazquez *et al.*, 2000; Chen *et al.*, 2002):

$$\omega = \left(\frac{NRT}{h}\right) \exp(-\Delta G_d / RT) \exp(-\Delta G_c / RT) \quad (3)$$

In the Eq. (3), ω is the nucleation rate, which is the reciprocal of the induction time of nucleation (τ), N is the Avogadro number, R is the gas constant per molecule, h is the Planck constant, T is the temperature. ΔG_d is the Gibbs free energy of volume diffusion and ΔG_c is the Gibbs free energy of nucleation.

The main barrier of 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 ΔG_d can be replaced by αΔS/R, where α is the molecule quantity that should be in the right conformation for incorporation in a nucleus, ΔS is a decrease of entropy on crystallization of 1 molecule TAGs (ΔS = ΔH/T) (Kloek *et al.*, 2000).

Meanwhile, the Gibbs free energy of nucleation (ΔG_c) is associated with surface free energy in the crystal-melt interface (σ) and degree of effective super-cooling (ΔT) Eq. (4):

$$\Delta G_c = \left(\frac{16}{3}\right) \frac{\pi\sigma^3(T_m^0)^2}{(\Delta H)^2(\Delta T)^2} \quad (4)$$

where, ΔH is heat of fusion. The degree of effective super cooling is defined as the difference between equilibrium melting Temperature (T_m⁰) and the crystallization Temperature (T_c). The equilibrium melting temperature is widely used to describe the characteristics of a multi-component system and the polymer (Hiromi, 1993). The magnitude of T_m⁰ was established following the procedure described by Hoffman and Weeks (1962). Thus, the apparent melting temperature T_m vs. T_c plot provided a straight line whose crossing point with the line T_m = T_c represented T_m⁰. Therefore, the Eq. (3) can be rewritten as follows:

$$\tau^{-1} = \omega = \left(\frac{NRT}{h}\right) \exp\left(\frac{-\alpha\Delta S}{R^2T}\right) \exp\left[-\left(\frac{16}{3}\right)\left(\frac{\pi\sigma^3(T_m^0)^2}{(\Delta H)^2RT(\Delta T)^2}\right)\right] \quad (5)$$

After mathematical rearranging, the Eq. (5) was rewritten as Eq. (6) which can deduce the relation of induction time and temperature by using natural logarithm:

$$\ln \tau T = \ln \frac{h}{NR} + \alpha \frac{\Delta S}{R^2 T} + \left(\frac{16}{3}\right) \frac{\pi \sigma^3 (T_m^0)^2}{(\Delta H)^2 RT (\Delta T)^2} \quad (6)$$

As can be seen from Eq. (6), the linear regression with a positive slope K can be obtained from the plot between $\ln \tau T$ and $1/T (\Delta T)^2$. Thus, the Eq. (4) can be simplified to Eq. (7) and the Gibbs free energy of nucleation is calculated:

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

After gaining ΔG_c and substituting into Eq. (3), the ΔG_d can be calculated.

RESULTS AND DISCUSSION

Equilibrium melting Temperature (T_m^0): In Fig. 1, the equilibrium melting Temperature (T_m^0) of palm oil and its mixtures was obtained according to the Hoffman-Weeks method and it shows a good linearity of the data plots ($R^2 > 0.85$). The equilibrium melting temperature of the pure palm oil and mixtures with 0.01, 0.05 and 0.1%, respectively span 85 level are 30.35, 32.98, 48.52 and 31.55°C, respectively. The study found that the equilibrium melting temperature of palm is always higher than the practical melting point obtained from the experiments (T_m). This could be explained that T_m^0 is the calculated melting point of the complete crystalline state, but T_m is related to the formed crystals under the applied experimental conditions.

Figure 1 shows that the additive of span 85 led to an increase in equilibrium melting temperature of mixtures, especially the level of 0.05%. This indicates the presence of molecular interaction between palm oil

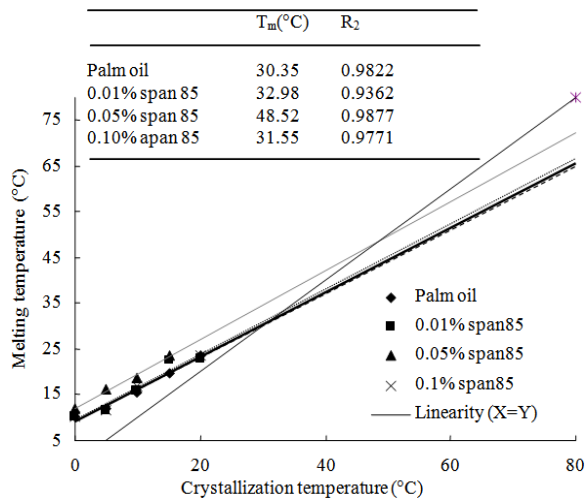


Fig. 1: Determination of equilibrium melting temperature according to the Hoffman-Weeks method
 T_m^0 : Equilibrium melting temperature

and span 85 (Runt *et al.*, 1984). And the trends of equilibrium melting temperature first increase and then smaller with the increase of span 85 level. Runt and Runt (1983) thought that the as-formed crystal molecules in mixtures may be to restructure and become harder molten state.

Isothermal crystallization kinetics: In Fig. 2, the coordinate point represents the actual percentage of crystallization and the solid lines are drawn based on Gompertz model. And Fig. 2 shows the kinetic model fitting to the crystallization data of palm oil mixture in the presence of span 85.

It is obvious to see that the span 85 additive not only prolongs the induction time, but also the crusting over time be delayed. Especially, the effect of the span 85 at 0.05 and 0.1%, respectively concentration levels is more prominent and the fat crystallization rate is relatively low under the experimental conditions. In the simulation conditions, the crystallization rate of palm oil added 0.1% span 85 is about 91% when palm oil is completely crystallization.

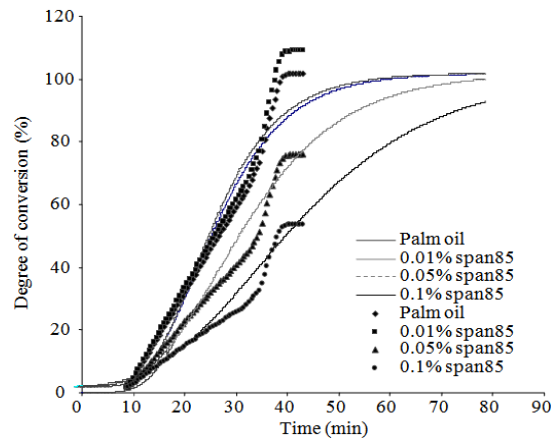


Fig. 2: Gompertz model fitted to the crystallization data of palm oil and mixtures at the crystallization temperature

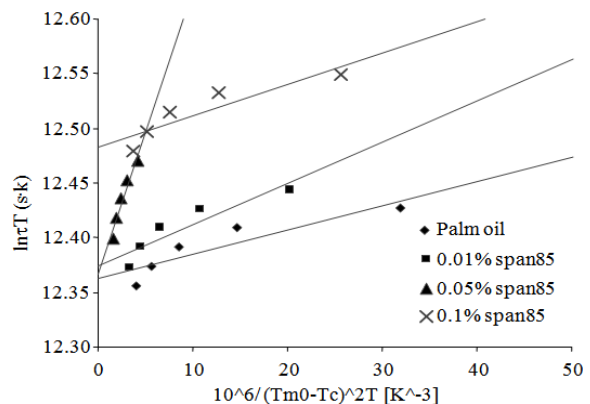


Fig. 3: Fisher-Turnbull model fitted to the nucleation data of palm oil and mixtures

Table 1: Kinetic particular quantified by the Gompertz and Fisher-Turnbull equations

Crystallization temperature (K)	Span 85 (% w/w)	ν (%/min)	τ (min)	R^2 fisher	Slope K fisher	ΔG_c (J/mol)
273	0.00	3.89	14.19	0.8664	0.0018	1.620
278						2.330
283						3.610
288						6.350
293						13.970
273	0.01	4.13	14.43	0.8959	0.0031	2.370
278						3.290
283						4.880
288						7.970
293						15.300
273	0.05	2.80	14.81	0.8812	0.0023	0.812
278						1.010
283						1.290
288						1.700
293						2.350
273	0.10	1.93	16.04	0.9641	0.0223	18.630
278						26.300
283						39.920
288						67.690
293						139.980

The same to be seen in Fig. 3, a good linearity of the plot of the Fisher-Turnbull model and the experimental data indicated that the nucleation kinetics of the fat systems containing span 85 additives can be characterized by the Fisher-Turnbull equation. The kinetic parameters and the correlation coefficient of the kinetic model were summarized in Table 1.

In Table 1, the induction time of nucleation increased with the additive span 85. This is in agreement with previous studies investigated through spectrophotometry method (Jia *et al.*, 2013), which showed that the nucleation is slower in a palm oil system containing span 85 compared to a pure palm oil. Thus the conclusion that span 85 additive has inhibition effects on the nucleation of palm oil can be obtained. At 0.01% span 85 level, however, the additive can delay the crystallization induction time, but it can also increase the nucleation rate of palm oil. In contrast, the nucleation rate can be reduced effectively at 0.05 and 0.1% span 85 level and in particular at 0.1% span 85 level, the additive can reduce the nucleation rate of doubling of pure palm oil. So far, the reasons the span 85 can delay the induction time and suppress nucleation rate have not been found, but according to the large difference between span 85 and palm oil molecular structure, so the some parts of additive may interfere the nucleation process which lead to significant inhibition (Hartel, 2001). The data of ΔG_c show that the higher the crystallization temperature is, the slower the nucleation is and the addition of amount of span 85 increased ΔG_c of palm oil except the 0.01% concentration span 85. The larger value of Gibbs free energy implies that the induction time of nucleation is longer and the nucleation rate idea slower in a system containing additives with 0.01 and 0.1% span 85 compared to a pure palm oil. Therefore, the conclusion span 85 additives can restrain nucleation is established.

CONCLUSION

Summarizing the results, it can be concluded as follow.

The isothermal crystallization kinetics of the palm oil and mixtures with span 85 additives can be successfully characterized by using the Gompertz model and the Fisher-Turnbull equation. The kinetic parameters on the induction time (τ), the crystallization rate (ν), the equilibrium melting Temperature (T_m^0) and Gibbs free energy can be obtained via the Gompertz equation, the Hoffman-Weeks method and Fisher-Turnbull equation.

The application of the span 85 can raise the equilibrium melting temperature of palm oil, this result implies that the crystal structure get an enhancement, but the concrete reason need to be studied further and deep.

The addition of span 85 additives can delay the induction time of nucleation, the nucleation rate also is reduced at 0.01 and 0.1% span 85 levels, but the effect of 0.05% span 85 is contrary. This is in agreement with previous spectrophotometry studies (Jia *et al.*, 2013). But the crystal is not complete in the system containing span 85 additives compared to the pure palm oil.

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