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Influence of Sorbitan Trioleate on Crystallization Kinetics of Palm Oil

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Abstract. Sorbitan trioleate(span 85) was added to palm olein at 0.01%, 0.05% and 0.1%(w/w). The crystallization kinetics of the mixture was studied by spectrophotometry. Avrami equation was used to build model and simulate the crystallization process. The span 85 and temperature may have some delay on the crystallization. Homogeneous nucleation and one-dimensional growth are the main nucleation in the crystallization process.

Keywords: palm oil; crystallization kinetics; absorbance; Avrami equation; span 85

1. Introduction

Palm oil is widely used in the oil and fat product field. As we know that the palm olein is liquid at normal temperature but it becomes turbid when temperature falls to 20℃. Its actual conditions of weatherability and transport are changeable because of the different climates in different counties and areas. So cyclic heating is used during the transportation, and then the speed of oxidative rancidity increases and the palm oil's storage time and quality are greatly influenced.

In order to solve the problems of margarine's harden and chocolate's stability that based on the palm oil during the storage period, studies about the influence of additives on palm oil's crystal behavior turns to focus. Studies show that trace amounts of additives can improve the oil's weatherability. Influences of palm oil diglycerides on palm triglycerides' crystallization are reported by Sew and Ng [1]. As additives, palmitic acid and monoglyceride have some impact on palm oil's crystallization kinetics [2]. Saberi [3] also pointed out 5% palm oil diglycerides decreased the nucleation rate of palm oil.

This paper shows the effect of sorbitan trioleate (span 85) on the crystallization of palm oil. Span 85 contents in palm oil range from 0.01 % to 0.1 %,and temperatures varies from 16 ℃ to 21 ℃.The changing rule of palm oil's crystallization can be showed by the samples' change of absorbance. Avrami equation is also used to imitate the whole crystallization, relevant mathematical model can be established, and the parameters (n, k) we get can tell us the mechanism of crystal growth and the crystal shapes.

2. Experimental

2.1. Apparatus

The apparatus mainly consists of heating and temperature controlling system (4 in Fig.1) and double beaker. The system was controlled by the temperature controller (1 in Fig.1). And the interlayer of double breaker (2 in Fig.1) was filled with circulating water whose temperature can keep stable in a long time.

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Cuvettes (3 in Fig.1) full of palm oil were placed in the double beaker. And the height of water in the beaker should not exceed the cuvettes.

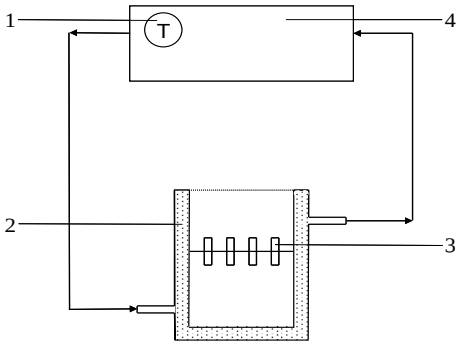

Fig. 1: Schematic of the apparatus: (1) the temperature controller; (2) the interlayer of double breaker; (3) Cuvettes; (4) temperature controlling system.

2.2. Materials and methods

Refined 24 ℃ palm oil was used in this work. Sorbitan trioleate (span 85) was used as the additive. Span 85 was mixed with the pure palm oil, melted at 80 ℃ and then maintained at that temperature for 30 min to make samples. The concentrations of span 85 were 0.01 %、0.05 % and 0.1 %(w/w).The samples should be stored in the thermostat at about 24 ℃. And the process parameters were summarized in the Table 1.

Tab.1 Experimental conditions

Temperatures of circulating water system /℃	Concentrations of span 85/ %	Indoor temperature /℃
16	0.01	
19	0.05	25
21	0.10	

3. Methods of Data Processing and Analysis

3.1. Kintics measurement

The absorbances of the samples were measured in a spectrophotometer at intervals. And the wavelength was about 600 nm instead of 500 nm in order that the method could be applicable to crude palm oil whose carotenes absorb at 446 nm [1]. Results were plotted graphically to express the crystallization of palm oil.

3.2. Establishment of mathematical model during the crystallization

Avrami equation (Eq.1) was used to simulate the course of crystallization [4]. The half period of the crystallization was measured by Eq.2:

$$X_t = 1 - \exp\left(-kt^n\right) \tag{1}$$

Where X_t is the relative absorbance, k is the crystallization rate, n is the Avrami index, t is the crystallization time

$$t_{1/2} = \left(0.693/k\right)^{1/n} \tag{2}$$

Avrami equation is the common mathematical model to imitate the crystallization of oil and fat. It is suitable for one crystallization peak oil system. Parameters in the equation help us to know the crystallization

much more totally. Generally, the Avrami index *n* has relationship with the nucleation method and the mechanism of crystal growth. It equals to the space dimensionality of growth and the time dimension of the nucleation process. Details about the relationships between parameters and crystallization behavior can be fund fromTab.2.

Tab. 2 The relationship between Avrami parameters and crystallization behavior [4]

The mechanism of crystal growth \ Nucleation method	Homogeneous nucleation	Heterogeneous nucleation
One-dimensional growth (acicular crystal)	n=1+1=2	n=1+0=1
Two-dimensional growth (flat crystal)	n=2+1=3	n=2+0=2
Three-dimensional growth (spherical crystal)	n=3+1=4	n=3+0=3

4. Results and discussions

4.1. Crystallization of crude palm oil and the oil mixed with span 85 at different temperatures

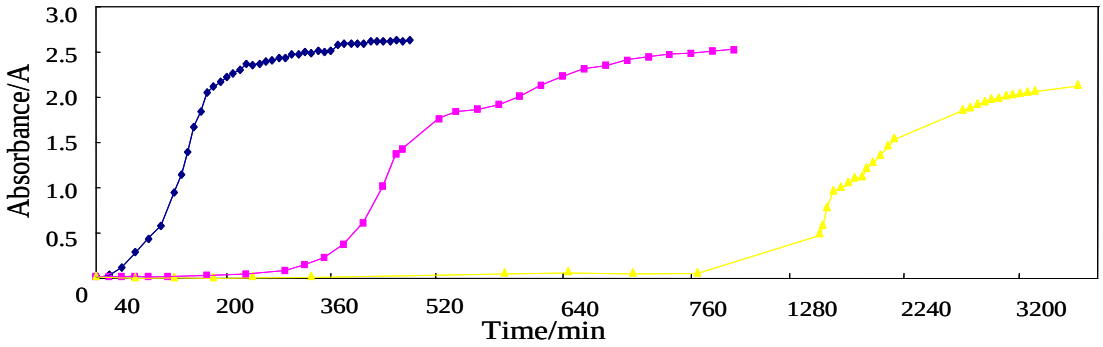

Fig. 2 Crystallization curve of crude palm oil under 16℃、19℃ and 21℃

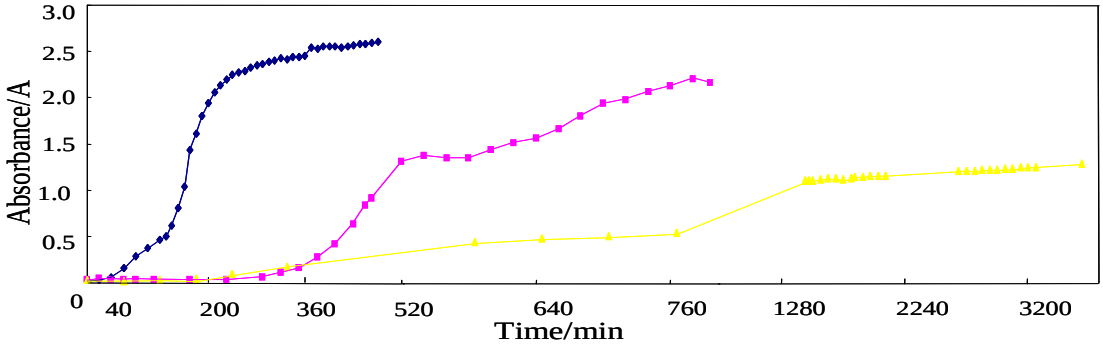

Fig. 3 Crystallization curve of palm oil with 0.01% span 85 level under 16℃、19℃ and 21℃

Crystallization of crude palm oil under different temperatures is showed by Fig. 2. Palm oil mixed with span 85 at 0.01%、0.05% and 0.1% levels is showed by Fig.3、Fig. 4 and Fig. 5 separately. Diamond or the blue curve (◆) refers to palm oil at 16℃, square or the red one (■) refers to 19℃ and triangle or yellow one（▲） refers to 21℃.Variation trend of three curves is the same, and the sigmoidal curve tells us four stages of crystallization: induction; nucleation; crystal growth and crusting over. The induction period is the lag time prior to the onset of crystallization that can be measured graphically at the point of a sharp increase in the absorbance [5].And it is obviously to find that proper warming can delay the crystallization of crude palm oil efficiently.

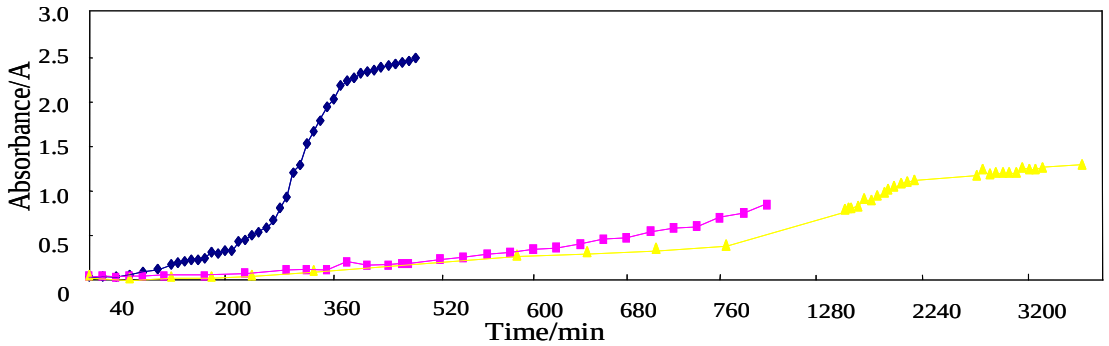

Fig. 4 Crystallization curve of palm oil with 0.05% span 85 level under 16℃、19℃ and 21℃

Variation trends of the three figures (Fig.3, Fig.4 and Fig.5) are similar to the crude oil (Fig. 2). Additions of span 85 have more or less delay effects on palm oil crystallization as a whole. Effect of span 85 at 0.1% level is the most obvious and 0.01% level is the least. But the exception is that crystallization of palm oil with 0.01% span 85 is promoted at 21℃ to some degree. Delay effects on crystallization also increase as the temperature increases. Palm oil with 0.1% span 85 level at 21℃ has the longest induction period in this experiment.

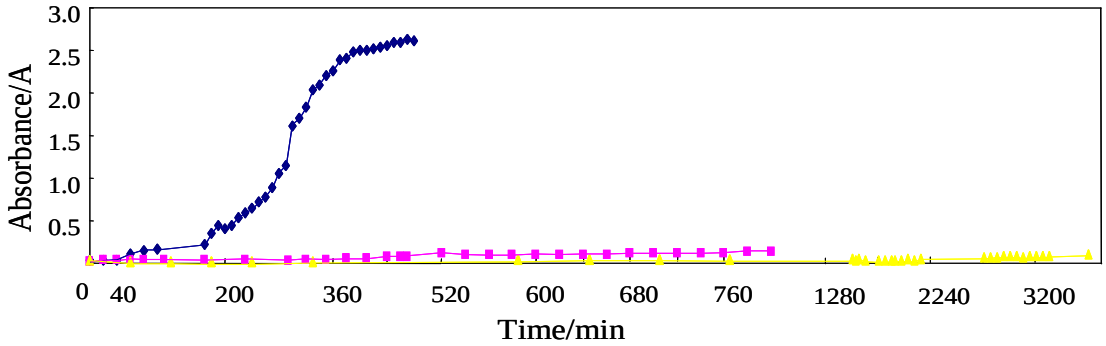

Fig. 5 Crystallization curve of palm oil with 0.1% span 85 level under 16℃、19℃ and 21℃

4.2. Mathematical model about the crystallization analysis of parameters

Mathematical model is built through Avrami equation and the simulated crystallization is showed by the following curves (Fig.6, Fig.7 and Fig.8). Blue lines (—) stand for crude palm oil, red lines(—) refer topalm oil with 0.01% span 85 level, yellow(—) is at 0.05% level and dark green ones(—) represent 0.1%.

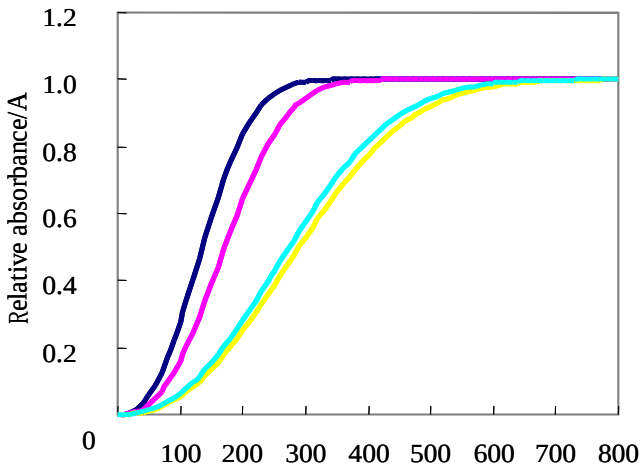

Fig. 6 Simulative crystallization of crude palm oil and oil with different concentration span 85 at 16℃

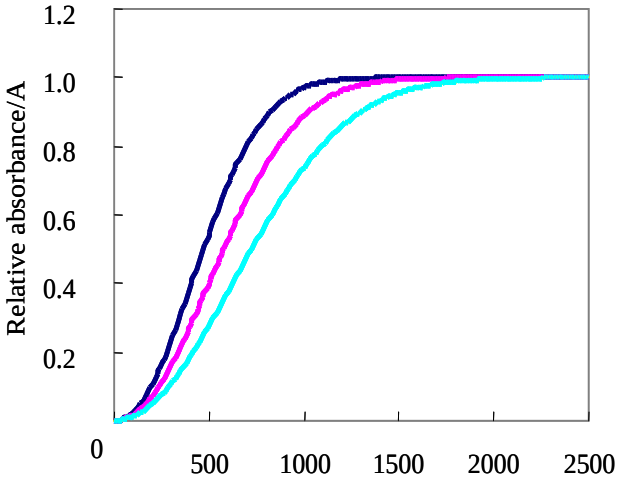

Fig. 7 Simulative crystallization of crude palm oil and oil with different concentration span 85 at 19℃

Simulative crystallization curves present typical sigmoidal type which really fit with the experiment results. Addition of span 85 brings extension to induction period and the crusting over time is also delayed. Effects of 0.05 % and 0.1 % are almost the same at 16 ℃ and 19 ℃, curves of 0.05 % and 0.1 % are even coincided at 19 ℃ (Fig.7). But exception appears at 21 ℃, 0.01% and 0.05% make crystallization advanced instead, delay effect still exist at 0.1% level.

Parameters of Avrami equation are showed in Tab.3.Values of *n* betweens 1 to 3, and most of them are 2 to 3.Homogeneous nucleation mainly happens during the crystallization of crude palm oil and most of palm oil mixed with span 85. Oil with 0.05% and 0.1% span at 21℃ are heterogeneous in the main position. But the nucleation method of oil with 0.1% span at 21℃ doesn't change, so changes of the nucleation method during crystallization may be the synthetic action of temperature and concentration of span. And further study is needed to find the key factor and the reason.

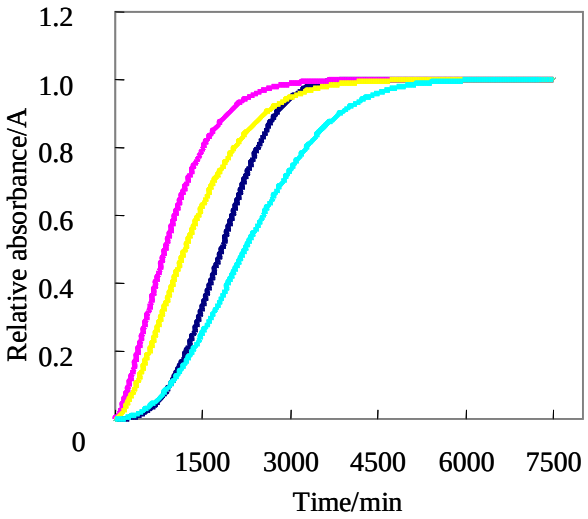

Fig. 8 Simulative crystallization of crude palm oil and oil with different concentration span 85 at 21℃

Acicular crystal is the main crystal morphology of this crystallization refers to Tab.2 and secondary crystallization may existence because of the non-integer value of n. Crystallization rate decreases with the increases of concentration on span 85 and the temperature in a specific range. Exorbitant concentration and temperature may bring opposite effect in the delay of crystallization. The half time of crystallization ($t_{1/2}$) corresponds to 50% of its growth after nucleation and can be determined graphically by subtracting the induction period from the time that is needed for 50% absorbance [5]. Oil with 0.1% span at 19℃ need the longest time for the 50% absorbance from Tab.3.

Tab. 3 The parameters of Avrami equation during the crystallization of palm oil

	Crude oil			Oil with 0.01% span			Oil with 0.05% span			Oil with 0.1% span		
Temperature/℃	16	19	21	16	19	21	16	19	21	16	19	21
Crystallization rate (*k*)	3.38 E-06	1.29 E-06	3.81 E-05	1.39 E-06	1.08 E-06	1.38 E-02	1.02 E-06	9.89 E-07	6.12 E-03	1.28 E-06	7.70 E-07	2.48 E-04
Crystal morphology (*n*)	2.49	2.14	2.87	2.55	2.10	1.48	2.37	2.04	1.58	2.35	1.93	2.19
Half period ($t_{1/2}$)	1.36 E+02	4.70 E+02	3.04 E+01	1.71 E+02	5.77 E+02	1.42 E+01	2.90 E+02	7.23 E+02	2.00 E+01	2.74 E+02	1.223 E+03	3.72 E+01

5. Acknowledgements

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