Rheological properties and phase change behaviors of coconut fats and oils

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ABSTRACT

The rheological properties of three commercial coconut fats and structure analysis during their solid-liquid and liquid-solid phase change were investigated. Dynamic viscosity of fluidized coconut fats, phase change profiles obtained from oscillation test with determined melting and crystallization temperatures were discussed and compared to the results obtained from DSC.

INTRODUCTION

Coconut fat is one of the major ingredients for the food production in Southeast Asia and also famous in European countries in both food and non-food industries. Generally, coconut fats belong to the unique group of vegetable oils called lauric oil about 44 – 51 %. Lauric acid ($CH_3(CH_2)_{10}COOH$) is known as small molecule fatty acid (< 14:0) which contains short or medium chain of saturated fatty acid. Other chemical compositions of coconut oil belong to myristic acid (16 – 19 %), caprylic acid (9.0 – 9.5 %), palmitic acid (8.0 – 9.5 %), oleic acid (5 – 6 %), capric acid (5 – 10 %), steric acid (3.0 – 3.5 %) and linoleic acid (1.0 – 1.5 %), respectively[1,2]. More than 90 % of fatty acids of coconut oil are saturated.

The physical properties aspect of oils and fats which is most important for functionalities in food processing is the solid-liquid and liquid-solid phase change and their flow behavior. Over the past years, their phase changes were measured mainly by Differential Scanning Calorimetry (DSC)[3,4]. Assumed by this research, rheology might be a practical method to define melting and crystallization temperatures with a great deal of information regarding its flow behavior and structural change during thermal transition. Therefore, the aims of this study were to determine rheological parameters during cooling and heating processes by steady shear and oscillatory shear and to compare with DSC results in the form of phase change profiles.

MATERIALS AND METHODS

Three commercial coconut fats studied were purchased from different sources; CF-1 (Palmin®, Peter Kölln KgaA, Elmshorn, Germany), CF-2 (Patum Vegetable Oil Co., Ltd., Bangkok, Thailand), and CF-3 (KTC (Edibles) Ltd, Wednesbury, Sri Lanka).

Rheological measurements

Viscosity was measured as a function of shear rate using a MCR301 Rheometer (Physica®, Anton Paar GmbH, Graz, Austria-Europe) with a double gap rotational cylinder. 8 ml sample were taken with the controlling temperature from 30 to 90 °C with $\Delta T = 10$ K. Samples were changed individually at each temperature. Shear rate was increased from 100 to 1500 /s in 2 min and then decreased from 1500 to 100 /s in 2 min. The data was collected every 4 sec at each state measurement. All data from the last state were calculated using a linear model. The flow behavior of coconut fats was explained according to Newton's equation.

From Newton's equation, dynamic viscosity (η_{dyn}) of coconut fats at different temperatures was used to calculate the flow activation energy (E_A) in J/mol using the well-known Frenkel-Eyring-equation (see Eq. 1).

$$\eta(T) = A \cdot \exp[E_A / RT] \qquad (1)$$

Where $\eta(T)$ is the dynamic viscosity at any temperature (Pas), A is a constant for a given system, R is the universal gas constant (J/mol·K) and T is absolute temperature (K).

The G′ (storage modulus) and G″ (loss modulus) were evaluated using a MCR301 Rheometer. 8 ml of samples were preheated at 50 °C for 5 min to be easily poured into measuring system. Three stepwise temperature sweeps were done by (1) cooling from 50 to 0 °C with a cooling rate of 0.5 K/min and then (2) kept at 0 °C for 30 min to ensure a complete crystallization. On the last period (3), samples were heated from 0 to 50 °C with the same heating rate. All measurements were done at least in duplicate.

Crystallization and melting curves were plotted using the universal software US 200 version 2.30. The transition temperatures were assigned based on the temperatures at which the changing of loss factor (tan δ = G″/G′) occurred. All definitions were given. T_1 indicates the first temperature at which samples start to melt which changing from solid-like (tan δ << 1), to mixed phase (tan δ = 1). T_2 points where the tan δ is lowest. T_3 points where changing from mixed phase to liquid-like (tan δ >> 1). T_4 indicates at which the samples completely melt.

Differential Scanning Calorimetry (DSC)

The experiments were done on a Simultan Thermo Analyse (STA409C, Netzsch Geraetebau GmbH, Germany). Oil samples were weighed into aluminium pans and hermetically sealed. Samples were then kept overnight below freezing point (− 20 °C) for subsequent DSC analysis. For analysis, samples were heated from -20 to 120 °C with two scanning rates of 2 K/min and 5 K/min, respectively. The instrument was calibrated with the standard procedure according to manufacturer user manual. However, the calibration can be done only with a scanning rate of 5 K/min, according to the equipment limitation. Nitrogen was purged and flowed with 75 ml/min. Each DSC scan was made with a new sample to ensure the same thermal history. All samples were at least in duplicate.

The manufacturer's software program was used to analyze and plot the thermal data. The melting transition temperatures were identified to each thermal curve, based on the temperature at which a change of the value of endothermic heat flow occurred (see Fig. 1). The onset temperature (T_{on}; point where the extrapolated basis line intersects the extrapolated slop in the first transition state.) and the offset temperature (T_{off}; point where the extrapolated leading edge of the last melting endotherm intersects with the basis line), the maximum temperature (T_{max}; point where the temperature is at peak or highest point of the curve), and the end offset temperature (T_{end}; point where the first temperature at which the curve become constant) were then determined. The end offset temperature indicates at which fat samples were completely melted.
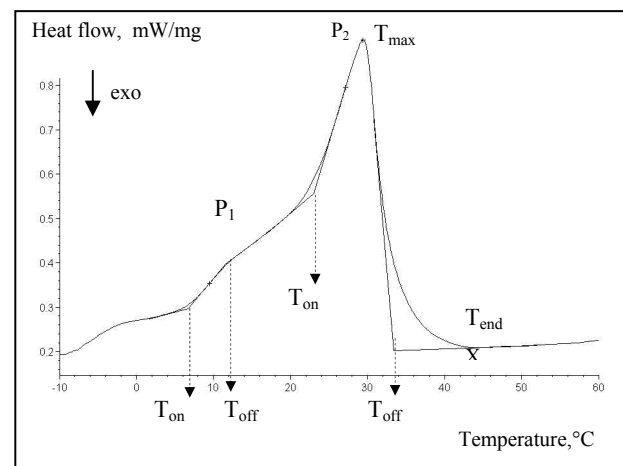

Figure 1. Differential scanning calorimetry (DSC) melting curve of coconut fat.

RESULTS AND DISCUSSION

Fluidized coconut fats or coconut oils were investigated in the temperature range of 30 – 90 °C. Flow curves were plotted and considered under the first law model. Over a wide range of shear rate studied, it was clear that fluidized coconut oils are subjected to Newtonian behavior which is independent from shear rate (1/s) (see Fig. 2).
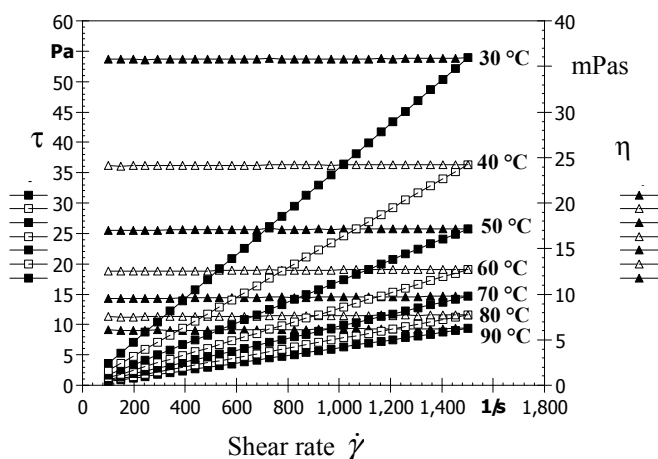

Figure 2. Flow curve of coconut oil in a temperature range of 30 °C to 90 °C

Dynamic viscosity (η_{dyn}) of three different coconut oils is summarized in Table 1. The results revealed that all coconut oils showed approximately the same η_{dyn} at the same temperature, even coconut oils obtained from different sources and refine processes. It can be concluded that viscosity of coconut oils are independent on sources and processes while strongly depend on temperature. As shown in Table 1, the higher temperature applied, the lower dynamic viscosity exhibited. With increasing temperatures from 30 to 90 °C, dynamic viscosity of coconut oils decreased about 30 mPas. During a short range of temperature (30 – 50 °C), the dynamic viscosity was substantial decreased into more than a half of its original.

Comparison to other sources of saturated fat such as animal fats, e.g. fluidized lard and goose fats, coconut oils showed lower viscosity at the same temperature range (30 – 90 °C). Lard and goose dripping gave dynamic viscosity of 42.83 (35 °C) to 8.86 (90 °C) mPas (lard) and of 50.15 (30 °C) to 8.75 (90 °C) mPas (goose)[5]. It provides the evident that the saturated fat in coconut oils was unique with more short chain fatty acid than saturated fatty acid found in other sources of saturated fats.

Table 1. Dynamic (Newton) viscosity of coconut oils at different temperatures

T (°C)	Dynamic viscosity (η_{dyn})[a,b] mPas		
	CF 1	CF 2	CF 3
30	35.4	36.6	35.8
40	23.8	24.7	24.2
50	16.9	17.4	17.1
60	12.4	12.8	12.6
70	9.5	9.8	9.6
80	7.5	7.7	7.6
90	6.0	6.2	6.1

[a] Each value in the table represent the mean. Standard deviations of the reported results are less than 0.01.
[b] r of the reported results are more than 0.999.

The dependent of dynamic viscosity on temperature were further study using the well-known Frenkel-Eyring-equation. Flow activation energy (E_A) of coconut oils was calculated with the highest R^2 of 0.999 (see Table 2). All coconut fats showed no difference of E_A.

Table 2. Frenkel-Eyring-equation and flow activation energy of coconut oils

Sample	Frenkel-Eyring-equation	E_A kJ/kmol·K
CF 1	$\eta(T) = 7.776 \cdot 10^{-7} \exp[3234.9/T]$	26312.68
CF 2	$\eta(T) = 7.607 \cdot 10^{-7} \exp[3252.5/T]$	26455.84
CF 3	$\eta(T) = 8.061 \cdot 10^{-7} \exp[3228.5/T]$	26260.62

For solid-liquid and liquid-solid phase change behavior of coconut fats, the change in storage (G′) and loss (G″) moduli during the melting and crystallization period were investigated. The loss factor (tan δ) were determined which indicated if elastic or viscous property predominate in sample.

Table 3. Transition temperatures at each peak of coconut fats during heating process

Sample / Method	Heating rate (K/min)	Transition temperature (°C)[a,b]					
		Peak 1		Peak 2			
		Onset temp	Offset temp	Onset temp	Peak temp	Offset temp	end temp
CF 1							
DSC	5	6.2 ±0.8	11.1 ±0.7	22.2 ±1.1	28.3 ±1.6	32.0 ±2.1	40.5 ±3.5
	2	4.0 ±2.2	8.2 ±1.1	20.3 ±0.3	26.2 ±0.8	28.5 ±1.0	33.0 ±0.0
Oscillation		-	-	16.7 ±3.2 (T_1)	25.5 ±0.0 (T_2)	29.3 ±1.1 (T_3)	32.0 ±0.0 (T_4)
CF 2							
DSC	5	3.7 ±1.0	10.9 ±0.4	22.3 ±0.1	29.3 ±0.1	33.0 ±0.0	45.0 ±0.0
	2	1.1 ±0.6	9.5 ±1.9	19.1 ±0.1	26.7 ±0.4	29.2 ±0.4	34.0 ±0.0
Oscillation		-	-	19.4 ±0.7 (T_1)	26.0 ±0.0 (T_2)	27.5 ±0.7 (T_3)	30.0 ±0.0 (T_4)
CF 3							
DSC	5	7.4 ±1.3	11.9 ±0.5	22.4 ±1.3	29.6 ±1.6	33.5 ±2.1	42.5 ±3.5
	2	4.0 ±1.0	8.1 ±0.8	20.6 ±0.5	26.4 ±0.0	28.5 ±0.0	34.0 ±0.0
Oscillation		-	-	18.9 ±0.7 (T_1)	25.2 ±0.4 (T_2)	28.50 ±0.0 (T_3)	29.8 ±0.4 (T_4)

[a] mean ± sd; [b] (-) means No data related

Each transition temperature was identified at each peak where the change of loss factor occurred (see Table 3 and Fig. 3).

Considering the temperature range from T_1 to T_4, coconut fat showed the melting range of 17 – 32 °C (CF-1), of 19 – 30 °C (CF-2 and CF-3), respectively. In comparison with the same method, coconut fats showed the smaller range of melting temperature than other types of fats, ex. lard (24 – 47 °C) and goose fat (10 – 38.5 °C) reported by Hildebrandt and Senge[5]. This rapid change in coconut fat can be explained by the existence of lauric acid. Lauric acid contains short chain fatty acid (C12:0) and saturated which has a specific melting property with a small range of temperature for phase change solid-liquid and liquid-solid. This affected coconut fats to exhibit a small range of temperature for their phase changes.

In comparison, the transition temperatures obtained from oscillatory test were found well correlated and comparable to the transition temperature obtained from DSC. As expected, T_1, T_2, T_3, and T_4 were related to the onset-, peak, offset- and end temperature observed from the second peak of DSC. Additionally, it was close to those obtained from DSC at the scanning rate of 2 K/min. The same range of melting transition between these two methods was found.

However, data from rheometer promoted not only the change in tan δ but also in G′. As shown in Fig. 3, from 7 to 17 °C, slightly increased in G′ was observed. As considered as the beginning of melting process, this transition temperature was close to those obtained from first peak of DSC. Two or more peak curves have been observed due to the composition of various fatty acids in coconut fat. Oleic acid (C18:1) which has melting range of 5.4 to 7.4[6] may response to the first peak of melting curve. The second peak can be attributed to the predominant of lauric acid which has higher melting range of 45.9 to 50.3[6].
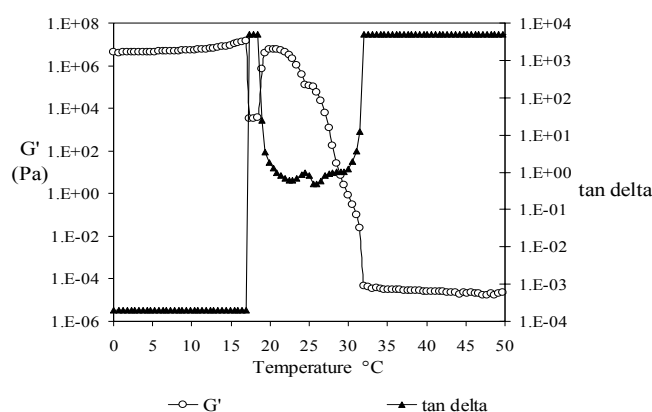

Figure 3. Comparison of melting behavior of coconut fat with tan δ and G′ in dependence on temperature.

Regarding to Fig. 1, all DSC curves also illustrated the complexity of the endothermic behavior of coconut fats which exhibit at least two peaks (P_1, P_2) during melting. The melting temperature of coconut fats can be determined as a range between onset- (T_{on}), offset- (T_{off}) and end temperature (T_{end}). As shown in Table 3, all types of coconut fats range the melting temperature approximately during 1 – 10 °C at the first peak and during 19 – 34 °C at the second peak based on the heating rate of 2 K/min and during 22 – 45 °C based on the heating rate of 5 K/min.

Comparing the three types of coconut fats, small difference of the transition temperature during the first peak occurred whereas the transition temperature range between onset- and offset temperature during the second peak showed relatively the same temperature range between three fats. It can be noticed that all samples showed the same melting temperature at the same heating rate.

However, when the heating rate increased from 2 to 5 K/min, all the melting temperatures increased, where the location of the melting peak shifted to higher temperature (Table 1). It can be concluded that a high heating rate results in higher melting point. Accordingly, the maximum peak temperature (T_{max}) which normally best describes the melting point of coconut fats increased about 2-3 degree with heating rate increased. It is the same about the end offset temperature (T_{end}), when the high heating rate was applied, slower the complete melting was reached. It can be explained that at higher heating rate, coconut fat requires more energy input (higher temperature) to achieve required melting enthalpy.

It is also possible to determine enthalpy values ($\Delta_{sl}h$) using manufacturer's software program for the calibrated samples at heating rate of 5 K/min. The results showed that $\Delta_{sl}h$ of all coconut fats studied were approximately the same values. Coconut fats gave $\Delta_{sl}h$ of 97 (CF-1), 102 (CF-2) and 100 (CF-3) kJ/kg, respectively.

For cooling process, rheological parameters were used to investigate the crystallization of coconut fat. Three types of coconut fats were observed the change in tan δ. The results showed that crystallization temperatures are relatively the same among coconut fats which range between 20.2 – 11.7 °C (CF-1), 19.5 – 10.4 °C (CF-2) and 19.2 – 9.7 °C (CF-3), respectively. In comparison with melting process, there is a large different between melting and crystallization temperatures where melting process showed longer process than crystallization and occurred at higher temperature range (see Fig. 4).

Considering the structural changes during melting/crystallization processes of coconut fats, dynamic oscillatory curves were plotted to present the change of rheological parameters (G′ and G″) as a function of temperature for all coconut fats (see Fig. 4). The same cooling/heating rate of 0.5 K/min was applied to all samples.

Fig. 4 illustrates the melting and crystallization profiles of the coconut fat (CF-1). During cooling process, melted coconut fat was filled in rheometer and then cooled from 50 to 0 °C. Fluidized coconut fat showed the viscoelastic "liquid" structure (G′ << G″). When the fluidized coconut fat start to crystallize, mixed phase occurred between viscoelastic "liquid" structure (G′ < G″) and viscoelastic "solid" structure (G′ > G″) and "cross over" of the moduli (G″ = G′ or tan δ = 1) changeably until it reached the end temperature which immediately changed to become crystallized coconut fat (G′ >> G″). The cooling process was maintained for 30 min to ensure the complete crystallized coconut fat was obtained.
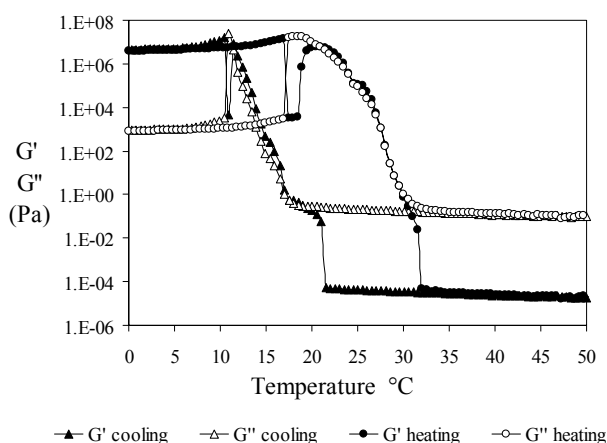
Figure 4. Comparison of melting and crystallization behavior of coconut fat in dependence on temperature.

During heating process, crystallized coconut fat showed a viscoelastic "crystalline" structure with $G' >> G''$. Coconut fat samples start to melt when the samples were heated and reached the first transition temperature (T_1 as shown in Table 3). At this temperature the crystalline structure start breaking down and become mixed phase characteristic. As same as crystallization process, when it reached the end temperature (T_4) coconut fat immediately changed the whole bulk to become liquid coconut oil ($G' << G''$). Interestingly, completely melted coconut fats ($> T_4$) showed absolutely the same G' and G'' values. It implied that after cooling and subsequent heating processes, melted coconut fats remain the same structure as its original which heating and cooling treatment do not differ the structural in coconut fats. It can be assumed that phase change process of coconut fat is reversible. Reason for such kind of transition is the predominant in coconut fats by the small and equal molecules of its fatty acid.

CONCLUSION
The rheological properties of three commercial coconut fats and their phase change behaviors during melting and crystallization processes were discussed. Modeling results showed that rheological properties of all coconut fats were characterized by Newtonian flow behavior over a wide range of temperature (30 – 90 °C). Physical properties of coconut fats depended strongly on temperature but not by its origin. At high temperature (> 35 °C), coconut oils are fluidized with substantial decreasing of dynamic viscosity when heated. At low temperature (0 – 35 °C), coconut fats showed viscoelastic properties where the structural changes depended on cooling/heating process.

During cooling/heating process, the rapid change of mixed phase between viscoelastic "liquid" and "solid" structure and cross moduli ($G' = G''$) was occurred. Interestingly, the completely melt coconut fats of both before and after cooling and subsequent heating showed the same G' and G'' values.

In this study, it was confirmed that the rheological measurement can be successfully used to evaluate structural changes and also to determine the temperature range during solid-liquid and liquid-solid phase change. Our results demonstrate that melting and crystallization temperatures obtained from oscillatory test are comparably to the values obtained from DSC measurement. These two methods provide useful information for phase change behavior and able to complete the results in itself. The results also are comparably. However, rheological measurements gave more ability to analysis the structure during phase changes which additionally able to study as a two-way method. At once, crystallization and subsequent melting can be evaluated simultaneously. On the other side, DSC is available to measure as a one-way method. Melting or crystallization processes can be determined only one at a time.

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