

Kinetics of Non-Isothermal Crystallization of Coconut-based Cholesteryl Ester: Avrami and Ozawa Approaches

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ABSTRACT

Kinetics of non-isothermal crystallization of coconut-based cholesteryl ester was performed by differential scanning calorimetry under various heating rates. Different analysis methods were used to describe the process of non-isothermal crystallization. The results showed that the Avrami equation could describe the system very well. However, the Ozawa analysis failed. A probable reason is the difference in the crystallization kinetics at high and low relative crystallization. The phase transitions of the coconut-based cholesteryl ester were also observed through optical polarizing microscopy.

INTRODUCTION

Coco-based cholesteryl ester is a thermotropic liquid crystalline material synthesized from esters of fatty acids extracted from locally available coconut oil. It is waxy and powdery at room temperature (Cureg, 2000). Cholesteryl ester is also known to exhibit two mesophases between the solid state and isotropic liquid state, namely the smectic phase and the cholesteric phase. This polymorphism of cholesteryl ester causes three phase transitions: crystalline to smectic, smectic to cholesteric, and cholesteric to isotropic. Unlike other liquid crystals, cholesteryl ester can exist as crystalline solid at room temperature. This will help in the investigation of crystalline to mesophase transitions, which is hard to achieve from most liquid crystals.

The most common approach used to describe the overall isothermal crystallization kinetics is the Avrami equation (Spruiell & Supaphol, 1999):

$$1 - X_t = \exp(-kt^n) \quad (1)$$

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where X_t is the relative degree of crystallinity, t is the duration of the crystallization process, n is the Avrami exponent, and k is the crystallization rate constant. The Avrami parameters n and k are constants typical of a given crystalline morphology and type of nucleation.

The constant k in Eq. (1) is given by:

$$k = \left(\frac{\pi}{3}\right) U^2 I \xi \quad (2)$$

where U is the rate of lateral growth, I is the rate of nucleation, and ξ is the average vertical extension of the crystals (Van Antwerpen, 1971).

Alternatively, Eq. (1) can be written in its natural logarithmic form

$$\ln[-\ln(1 - X_t)] = \ln k + n \ln t \quad (3)$$

Using Eq. (3), parameters k and n can be calculated from the least-square line fit of the double logarithmic plot of $\ln[-\ln(1 - X_t)]$ against $\ln t$ for each heating or

cooling rate, where k is the anti-logarithmic value of the y-intercept and n is the slope (Ziru He et al., 1997).

In the study of non-isothermal crystallization using Differential Scanning Calorimetry (DSC), the energy released during the crystallization process is a function of temperature rather than time as in the case of isothermal crystallization (Ziru He et al., 1997). Therefore, the relative crystallinity, X_t is given by:

$$X_t = \frac{\Delta H_T}{\Delta H_C} \quad (4)$$

where ΔH_T is the enthalpy of crystallization released during a temperature change and, ΔH_C is the overall enthalpy of crystallization, which is equal to the area enclosed by the crystallization peak in the DSC plot.

In order to use Eqs. (1) & (3) in non-isothermal conditions, the thermal lag of the sample and the DSC furnace is assumed to be minimal, such that

$$t = \frac{|T - T_o|}{\phi} \quad (5)$$

where T_o and T are the onset and the arbitrary temperature, respectively; t is the crystallization time; and ϕ is the heating or cooling rate (Ziru He et al., 1997).

Ozawa proposes another kinetic expression as an extension to Avrami's equation. Assuming that the non-isothermal process may be composed of infinitesimally small isothermal crystallization steps, the following equation has been derived:

$$1 - X_t = \exp \left[\frac{-K(T)}{\phi^m} \right] \quad (6)$$

where $K(T)$ (in °C/min) is the cooling/heating function, ϕ is the heating and cooling rate, and m is the Ozawa exponent, which depends on the dimension of the crystal growth (Ziru He et al., 1997).

To analyze the non-isothermal crystallization data, the natural logarithmic form of Eq. (6) is derived:

$$\ln \left[-\ln (1 - X_t) \right] = \ln K(T) - m \ln \phi \quad (7)$$

With different heating/cooling rates and plotting $\ln[-\ln(1-X_t)]$ against $\ln \phi$ at a given temperature, a straight line should be obtained. $K(T)$ and m are determined from the y-intercept and slope, respectively (Yuxian An et al., 1998).

Understanding the kinetics of crystallization, or any phase transition, gives further insight on what appropriate conditions a phase transition would occur. This would include the temperature at which transition occurs, heating or cooling rates, the amount of energy needed for a transition to happen, the ordering of molecules, and other parameters.

This research work aims to investigate the kinetics of the crystal to smectic phase transition of cholesteryl ester under non-isothermal conditions because it is usually under this condition that liquid crystals are used. Differential Scanning Calorimetry will be used with various heating rates, supplemented by microscope observations.

METHODOLOGY

The coconut-based cholesteryl ester used in this study was taken from the Liquid Crystals Laboratory of the UP Diliman Institute of Chemistry.

For calorimetric measurements, cell samples were prepared using solid crimp cells. Cholesteryl ester, in its solid form, was weighed in the sample cells with a net weight of 2.40 ± 0.01 mg. This sample weight is enough for the sensitivity of the Shimadzu DSC-50 equipment for thermal analysis. The crimped samples were heated using the DSC from 25°C to 100°C with various heating rates (1, 2, 3, 4, and 5°C/min). Analysis was done using the Thermal Analysis Program of DSC.

For microscopic investigations, a liquid crystal cell was prepared using two glass plates. The sample was then introduced through a gap by capillary method. The textures of cholesteryl ester at different temperatures

were observed and photographed using the BH-2 Olympus Polarizing Microscope equipped with crossed polarizers and camera attachment. Control of temperature was made using the Mettler Toledo FP90 Central Processor connected to a hot stage that can be mounted on the microscope stage.

RESULTS AND DISCUSSION

Non-isothermal crystallization kinetics based on Avrami equation

The DSC thermograms of cholesteryl ester at various heating rates are presented in Fig. 1. Table 1 shows a summary of the non-isothermal data gathered from the DSC.

The data presented in Table 1 reveal that the exothermic peak temperature T_p , which corresponds to the crystal to smectic phase transition, shifts to a higher temperature as the heating rate increases.

Moreover, the transition is faster at higher heating rates (Table 1) as shown by the peak crystallization time t_{max} , which is the amount of time elapsed from the onset of transition up to the peak temperature. This was taken using DSC TA analysis. The relative crystallinity at the peak temperature, X_{ip} ranges from 52.25% to 60.06%.

The relative crystallinity is determined by dividing a crystallization peak into small strips. Each small strip corresponds to the amount of heat involved in the crystallization process from the onset of crystallization up to a certain temperature, thus obtaining the relative crystallinity as a function of temperature. The results are shown in Fig. 2. All the plots of relative degree of crystallinity versus temperature have essentially the same pattern. At approximately 52.55% to 60.06% X_r , the shift to higher temperature of the transition peak as the rate increases is evident. In order for these data to be analyzed using the Avrami equation, the horizontal temperature scale must be transformed into the time domain using Eq. (5).

Fig. 3 shows the relative crystallinity as a function of time. The plots indicate that the faster the heating rate, the shorter the time needed for the completion of the

transition. The sigmoidal shape of the curves in Fig. 3 suggests that the Avrami analysis might be applicable to the non-isothermal data from the DSC.

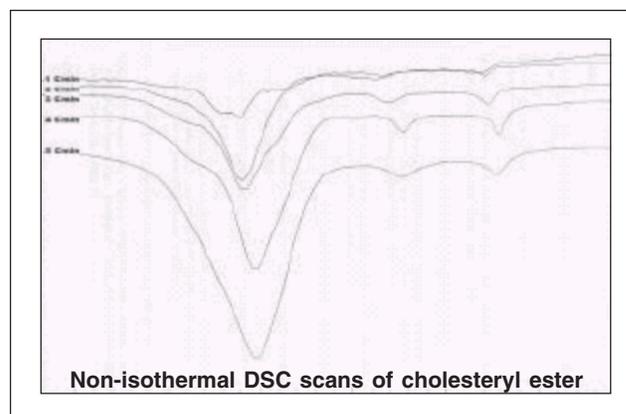


Fig. 1. DSC thermograms of cholesteryl ester at various heating rates.

Table 1. Parameters of cholesteryl ester during non-isothermal crystallization process.

ϕ (°C/min)	T_p (K)	t_{max} (min)	X_{ip} (%)	ΔH_c (J/g)
1	327.94	13.15	59.94	-50.81
2	328.09	8.55	54.19	-49.82
3	328.46	5.83	55.27	-59.38
4	329.49	4.54	52.55	-64.08
5	329.63	3.86	60.06	-57.64

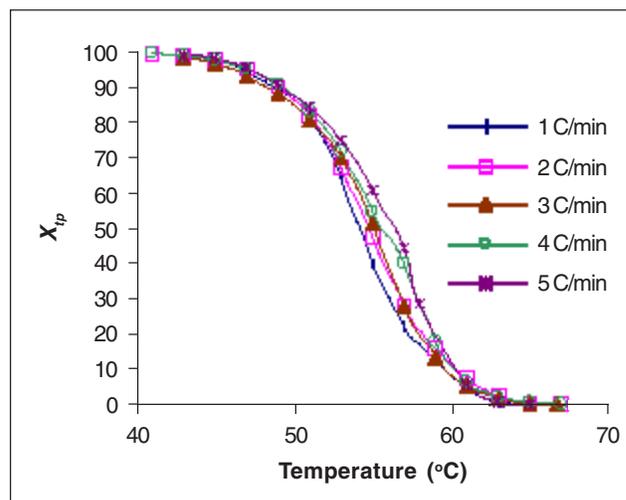


Fig. 2. Relative crystallinity as a function of temperature.

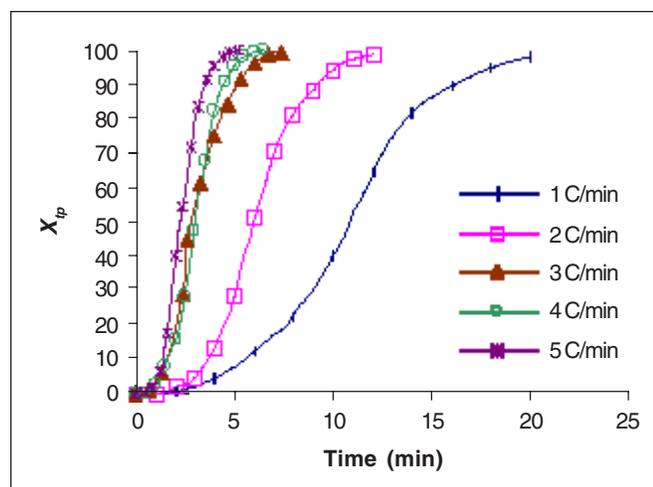


Fig. 3. Relative crystallinity as a function of time.

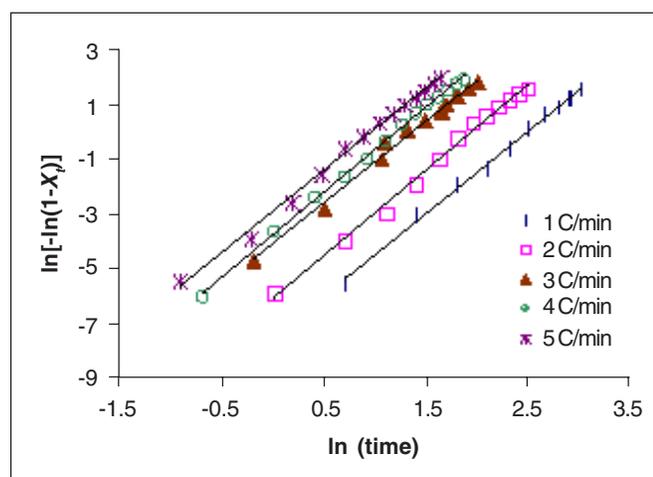


Fig. 4. Avrami analysis of the data shown in Fig. 3.

 Table 2. Parameters k and n for non-isothermal crystallization of cholesteryl ester.

ϕ (°C/min)	k	n	$t_{1/2}$ (min) $= (\ln 2/k)^{1/n}$	$t_{1/2}^{-1}$ (min) ⁻¹
1	5.67×10^{-4}	2.99	10.76	0.0929
2	2.27×10^{-3}	3.09	6.33	0.1579
3	1.69×10^{-2}	2.95	3.52	0.2839
4	2.21×10^{-2}	3.05	3.08	0.3247
5	5.12×10^{-2}	2.97	2.40	0.4167

Fig. 4 presents the Avrami analysis of the data shown in Fig. 3. It shows the plots of $\ln[-\ln(1-X_p)]$ versus $\ln t$ at various heating rates. The linearity maintained from the initial stages of transition until very high degree of conversion indicates that the Avrami equation correctly

describes the non-isothermal crystallization process of cholesteryl ester. From the slopes and intercepts of the lines in Fig. 4, the Avrami exponent n and rate constant k can be determined. Moreover, the half-time for crystallization $t_{1/2}$, which is analogous to t_{max} has been taken directly from Fig. 3. This is calculated as a function of parameters k and n . All the data are listed in Table 2.

Values of rate parameters show that the crystallization rate k increases with the increase of heating rate. This might have been caused by the effect of superheating as heating rate is increased (Yuxian An et al., 1998). These values of k , together with the values of $t_{1/2}^{-1}$, show that the rate of non-isothermal crystallization is proportional to the heating rate. The Avrami exponent is found to be ~ 3.0 , which suggests either a three-dimensional sporadic nucleation or a two-dimensional spontaneous nucleation. However, according to Price and Wendorff, the crystallization from a smectic mesophase is three-dimensional sporadic nucleation (Ziru He et al., 1997). Therefore, the first case is more probable.

Non-isothermal crystallization kinetics based on Ozawa equation

For comparison, Ozawa's model is used to deal with the data of non-isothermal crystallization. The plots at temperatures from 316 K to 336 K are shown in Fig. 5. Table 3 gives a summary of the slope and y-intercept values of the plots. The changing slopes indicate that m is not constant with temperature. One probable reason is the assumption of the Ozawa model. It must be noted that the X_t values chosen at a given temperature include the values selected from the earliest stage of the transition at high heating rate and the values from the end state at lower rate (<http://www.shodor.org/UNCChem/advanced/kin/arrhenius.html>). The kinetics of transition should be different at low- and high-relative crystallization. Also, shoulder transitions occur near the onset of the heating curves for rates 1, 2, 3, and 4°C/min. These shoulder transitions may be due to difference in the molecular dynamics of the sample when undergoing phase transitions. Thus, Ozawa analysis cannot adequately describe the non-isothermal crystallization of cholesteryl ester.

Optical microscopy

At room temperature, the cholesteryl ester is observed in its crystalline state (Fig. 6a). Upon heating, focal conic

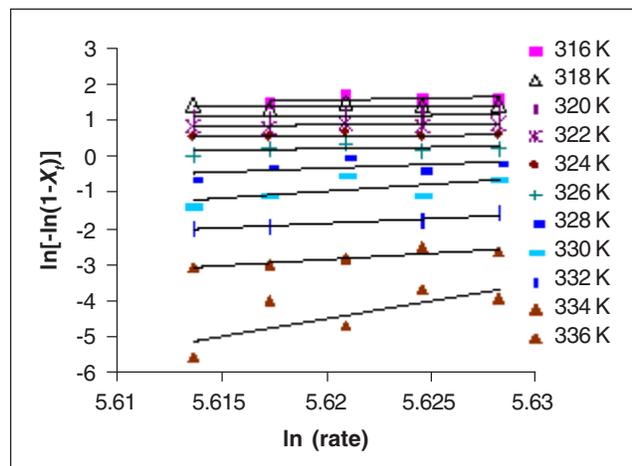


Fig. 5. Ozawa analysis of the data shown in Fig.3 at different temperatures.

Table 3. Slopes and intercepts for the Ozawa analysis.

Temperature (K)	Slope	Intercept
316	7.4012	-40.0370
318	0.4740	-1.2953
320	6.0744	-33.0340
322	6.1609	-33.7850
324	4.4005	-24.1760
326	8.8955	-49.8170
328	21.1370	-119.1500
330	39.2660	-221.6700
332	26.7010	-151.9200
334	36.3120	-206.9200
336	99.0850	-561.3500

texture (Fig. 6b) is observed before changing to the grandjean planar texture (Fig. 6c). This change in texture corresponds to the smectic phase and cholesteric phase, respectively. Further heating results in an isotropic phase (Fig. 6d).

CONCLUSION

Non-isothermal crystallization of coconut-based cholesteryl ester shows rate-dependent characteristics. The Ozawa analysis, when applied to this system, failed to provide a description of the non-isothermal crystallization. This failure is due to the assumption of this treatment. An alternative method based on the Avrami analysis was used. The non-isothermal crystallization data could be suitable over a wide range of relative crystallinities by using only two adjustable parameters. This method enables the calculations of crystallization rate parameters, which increase with increased heating rates, and half-time of crystallization, which decreases with heating rate. Observations using a polarizing microscope confirmed the crystal to smectic phase transition. The smectic phase was exhibited by the focal conic texture.

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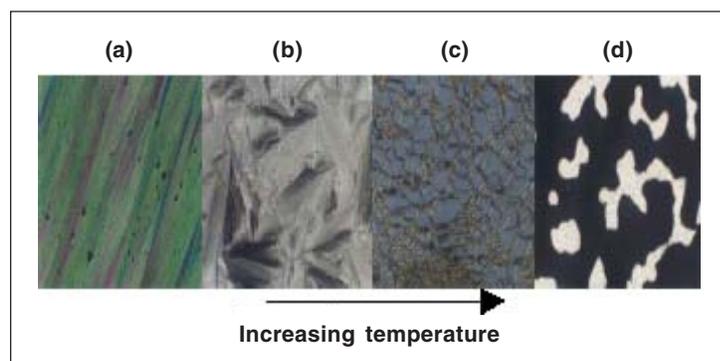


Fig. 6. Cholesteryl ester in its (a) crystalline state, (b) smectic phase, (c) cholesteric phase, and (d) isotropic phase.

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