

# On the Use and Misuse of the Avrami Equation in Characterization of the Kinetics of Fat Crystallization

Alejandro G. Marangoni\*

Department of Food Science, University of Guelph, Guelph, Ontario N1G2W1, Canada

**ABSTRACT:** The Avrami model is widely used in the analysis of crystallization kinetic data. Unfortunately, the use of the original model has been abandoned in favor of modified versions. The modifications are largely arbitrary and create a dependence between the Avrami constant and the Avrami exponent. From a curve-fitting point of view, no advantages exist in using the modified over the original form of the Avrami model. The order of a polynomial fit to crystallization data is not equivalent to the Avrami exponent. The use of turbidity measurements for the quantitative characterization of crystallization kinetics is not valid.

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**KEY WORDS:** Avrami equation, crystallization, kinetics, modified Avrami equation.

*The Avrami model and its "modification."* In the late 1930s and early 1940s, Michael Avrami developed a theory of the kinetics of phase change (1–3). The well-known Avrami equation (2) describes changes in the volume of the crystals as a function of time during crystallization, and has the general form:

$$F = \frac{V - V_o}{V_m - V_o} = 1 - e^{-Bt^k} \quad [1]$$

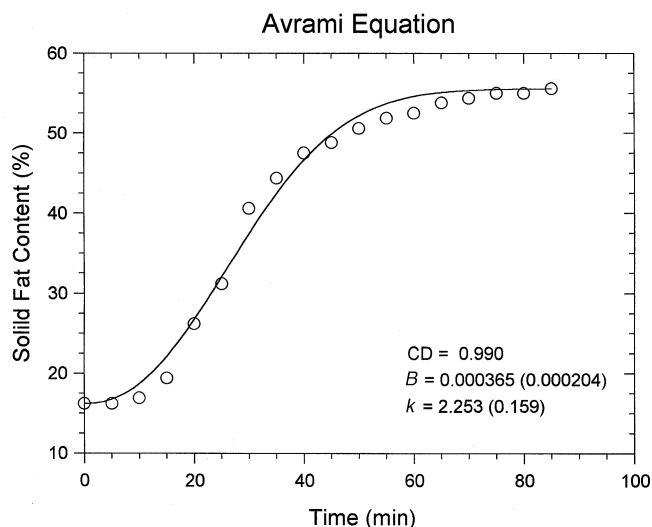
where  $V$  is the volume of the crystals,  $V_o$  is the initial crystal volume (usually zero),  $V_m$  is the maximal crystal volume attained after crystallization is complete,  $B$  is the Avrami constant, and  $k$  is the Avrami exponent. Of course, mass can be used instead of volume in Equation 1. This function is sigmoidal, with an initial lag-period, where crystallization occurs very slowly, followed by a rapid increase in crystal volume or mass. Eventually, all the material which was supersaturated crystallizes out and a plateau is reached (Fig. 1).

In the past, crystallization data were fitted to the linearized form of this equation by simple linear regression:

$$\ln[-\ln(1 - F)] = \ln(B) + k \ln(t) \quad [2]$$

Hence, a plot of  $\ln[-\ln(1 - F)]$  vs.  $\ln(t)$  has a slope of  $k$  and a y-intercept of  $\ln(B)$ .

\*E-mail: amarango@uoguelph.ca



**FIG. 1.** Nonlinear least-squares fit of the Avrami equation to palm oil crystallization data. CD, coefficient of determination;  $B$ , Avrami constant;  $k$ , Avrami exponent. Values in parentheses are the standard deviations of the parameter values.

Unfortunately, in 1988, Khanna and Taylor (4) arbitrarily suggested a modification of the Avrami equation to:

$$F = \frac{V - V_o}{V_m - V_o} = 1 - e^{-(At)^k} \quad [3]$$

These authors did not provide any theoretical justification for this "modification." This new function has nothing to do with the Avrami model and should not be called the "modified" Avrami equation. The only justification these authors provided was their opinion that  $B$  and  $k$  were correlated, and that this transformation would solve this problem. However, no proof of this was given in their paper.

The units of the Avrami constant  $B$  are  $t^{-k}$ , since the exponential factor must be dimensionless. What Khanna and Taylor (4) did was arbitrarily transform the Avrami constant from a complex constant of a  $k$ th order process to a first order rate constant with units of  $t^{-1}$ . Crystallization is not a first order process. Even though it may be nicer to report a first order rate constant in research papers, this does not justify this arbitrary modification.

The difference between the two functions lies in the exponential term:

$$e^{-(At)^k} = e^{-Bt^k} \quad [4]$$

taking the natural logarithm on both sides, one obtains:

$$-(At)^k = -Bt^k \quad [5]$$

which is equivalent to:

$$-A^k t^k = -Bt^k \quad [6]$$

dividing by  $t^k$  and multiplying by  $-1$  results in:

$$A^k = B \quad [7]$$

Hence, the “modified” Avrami equation constant  $A$  is the  $k$ th root of the Avrami model constant  $B$ :

$$A = B^{1/k} \quad [8]$$

Hence, the unjustified and arbitrary Khanna and Taylor modification (4) of the Avrami model creates a dependence of  $B$  on  $k$ , the problem that these authors were seeking to solve. These authors did not solve this problem at all—they may even have exacerbated it.

The Avrami and “modified” Avrami equations were fitted to literature-derived palm oil crystallization data [solid fat content (SFC) vs. time at 5°C] (5) by nonlinear regression using the software package Scientist 2.0 for Windows (Micromath Scientific Software, Salt Lake City, UT). In both cases convergence was achieved once suitable initial estimates for  $B$  and  $k$  had been found (Figs. 1 and 2), and no sensitivity to initial conditions was detected.

From a curve-fitting point of view, there are no differences between these two functions. Nonlinear least-squares fits of the Avrami and “modified” Avrami equations to crystallization data worked very well—convergence was readily achieved with no parameter value sensitivity to initial conditions. However, the “modified” Avrami equation has no theoretical foundation; therefore, the Avrami equation should be

used and their relationship to the Avrami equation. It has come to my attention that some researchers equate the order of a polynomial fit to crystallization data to the Avrami exponent  $k$ . This is not correct. An exponential function can be expanded into a power series. By expanding the Avrami equation into a power series, we obtain:

$$\begin{aligned} (V - V_o) &= (V_m - V_o) \left( 1 - e^{-Bt^k} \right) \\ &= (V_m - V_o) \left( t^k + \frac{t^{2k}}{2!} + \frac{t^{3k}}{3!} + \frac{t^{4k}}{4!} + \dots \right) \end{aligned} \quad [9]$$

We can compare this expression to a polynomial function:

$$(V - V_o) = (V_m - V_o) (a + bt + ct^2 + dt^3 + et^4 + \dots) \quad [10]$$

One can immediately notice that the Avrami equation series contains an extra  $k$  term in the exponent of each  $n$ th expansion term. Therefore, the dependent variable in the Avrami equation increases more steeply as a function of time than the dependent variable for a  $k$ -equivalent polynomial function (e.g.,  $k = 2$  and  $n = 2$ ).

We fitted polynomial functions to the crystallization data of Ng and Oh (5) and found that a fourth-order polynomial fitted the data significantly better than a second- or third-order polynomial ( $P < 0.05$ ) (Fig. 3). No significant differences ( $P > 0.05$ ) in the goodness-of-fit were observed using higher-order polynomials.

Therefore, an Avrami equation with an exponent of 2.25 (Fig. 1) is equivalent to a fourth-order polynomial equation (Fig. 3). When using polynomial functions to fit crystallization data, it is imperative to remember that the order of the polynomial function obtained from nonlinear fits to the data is not equivalent to the Avrami exponent—the order of the polynomial equation has no mechanistic meaning.

*The misuse of turbidity measurements to monitor fat crystallization.* Some recent research reports, appearing both in *JAOCs* and at AOCs meetings, include the kinetic characterization of crystallization using turbidity measurements. In particular, researchers have equated increases in the volume of crystallized material ( $V$ ) to increases in turbidity ( $\tau$ ):

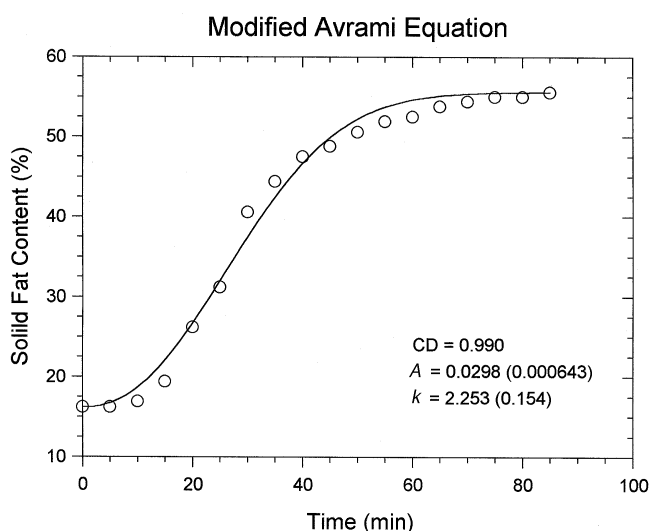


FIG. 2. Nonlinear least-squares fit of the “modified” Avrami equation to palm oil crystallization data.  $A$ , modified Avrami constant; see Figure 1 for other abbreviations. Values in parentheses are the standard deviations of the parameter values.

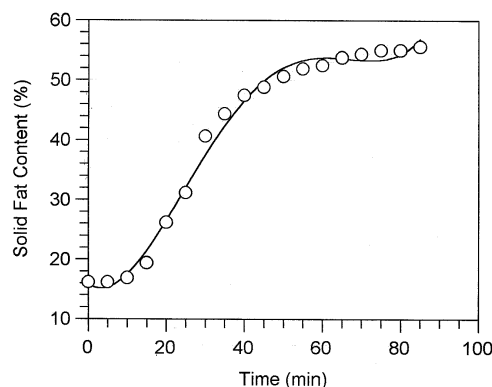


FIG. 3. Fourth-order polynomial fit to palm oil crystallization data.

$$F = \frac{V - V_o}{V_m - V_o} = \frac{\tau - \tau_o}{\tau_m - \tau_o} \quad [11]$$

The first problem with this assumption is that  $\tau_m$  is usually taken as the off-scale turbidity value. This maximal turbidity does not correspond to the end of crystallization, or the maximal volume or mass of crystallized material achieved. It simply represents the point at which the crystallizing material becomes too opaque, and the amount of transmitted light becomes negligible. However, the crystallization process continues well after the turbidity values have gone off scale. Without a true maximal turbidity value which corresponds to the end of the crystallization process, the Avrami equation cannot be used.

Secondly, zero angle scattering is proportional to the amount of mass, provided that no multiple scattering occurs, that is, particles are smaller than  $\lambda/20$  and are isotropic point scatterers, and that no absorption takes place. In this case:

$$\tau = \frac{16\pi}{3} R_{90^\circ} \quad [12]$$

where  $\tau$  is the turbidity at zero scattering angle and  $R_{90^\circ}$  is the Raleigh ratio at  $90^\circ$  and refers to primary scattering from unit volume of solution. Therefore, in the limit where the concentration of the scattering material goes to zero:

$$\frac{K_c}{R_{90^\circ}} = \frac{1}{M} \quad [13]$$

where  $K$  is a constant,  $c$  is concentration, and  $M$  is the mass of the crystals (6).

As particles become larger than  $\lambda/20$ , these assumptions do not apply. For example, if we use 600 nm light, the limit of applicability of turbidity measurements would be for particles 30 nm or smaller (6).

Thirdly, an observed decrease in transmitted light could be due to light refraction—an apparent change in velocity of the transmitted light beam as it travels through the sample. Fat crystals are extremely birefringent, and light is transmitted through them. This could cause significant refraction of the

incident light, and lead to a drop in the intensity of the transmitted light. This increase in turbidity would then have nothing to do with the volume or mass of crystals present in the sample.

For these reasons, turbidity measurements should not be used in the kinetic characterization of crystallization processes. Turbidity measurements are a good qualitative tool to study crystallization, but cannot be used for quantitative work, unless properly calibrated.

*Conclusions.* The Avrami equation should be used in its original form (Eq. 1) and the use of the “modified” Avrami equation should be abandoned. The order of polynomial functions fitted to crystallization data has no mechanistic significance. There is no need to use polynomial functions in the analysis of kinetic (data derived from) crystallization experiments. Measurements of the increases in crystal volume/mass during crystallization should be performed microscopically, or by SFC determinations, and not by turbidity measurements.

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