

Determination of Non-Isothermal Crystallization Rate Constant for *Pseudo-Experimental* Calorimetric Data

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In the present work, non-isothermal crystallization data in the form of heat flow vs. temperature curves were generated using the Nakamura Model and its typical parameters reported in the literature for polypropylene. The values obtained for these curves were added to experimental baselines of a DSC to introduce typical noises in the calorimetric traces generated. The Master Curve Approach was applied by one of the authors to retrieve the non-isothermal crystallization rate constant for these simulated curves without information about the conditions used to generate these *pseudo-experimental* curves. Thus, the applicability of the Master Curve Approach was tested for data perfectly described by the Nakamura Model. With this procedure, the authors were able to check the sensitivity of the method to uncertainties in the determination of the induction time. The results showed good agreement between the *pseudo-experimental* curves and the curves simulated using the retrieved non-isothermal crystallization rate constant. However, this good agreement was only possible due to a compensation effect, because some of the parameters showed significant differences between the *pseudo-experimental* and retrieved values. Among these parameters are the pre-exponential factor of the non-isothermal crystallization rate constant, the temperature of the onset of the crystallization process, and the initial degree of crystallinity of the differential form of the Nakamura Model. These problems were not caused by the Master Curve Approach, but by inherent difficulties in the DSC analysis.

Keywords: Master Curve Approach, non-isothermal crystallization, pseudo-experimental

1. Introduction

Some of the most important industrial polymers are semi-crystalline. This causes them to crystallize during the cooling phase of processing, affecting both properties and processing conditions. Therefore, it is important to incorporate the crystallization phenomenon in polymer processing simulation programs. However, one of the difficulties in incorporating the crystallization process in commercial software is the need for easy, fast and reliable methods for determining the parameters of the kinetic model chosen to describe the crystallization process.

In three previous works of the present authors, the Master Curve Approach proposed by Isayev et al.¹ was applied to calculate the non-isothermal crystallization rate constant $K(T)$ for modified polypropylenes^{2,3} (maleic anhydride and acrylic acid grafted polypropylenes) and for a heterophasic polypropylene sample (Polypropylene/Ethylene-propylene rubber PP/EPR)^{4,5}. The non-isothermal crystallization rate constant obtained by this method was used to calculate the curves of relative crystallinity as a function of temperature at different cooling rates. These simulated curves were highly consistent with the experimental data obtained by DSC. One of the major advantages of the Master Curve Approach is the possibility of using non-isothermal experiments, which allow for the determination of kinetic data at lower temperatures than if only isothermal experiments were used. Therefore, these data are more representative of the conditions in which crystallization takes place during polymer

processing. This proposition is still applied and accepted by publications of the highest level⁶⁻⁹.

The nonlinear regression method is being used as an alternative way of obtaining the parameters for kinetic crystallization models, such as Nakamura's^{10,11}, Kamal and Chu's¹², and Dietz¹³ and Malkin's¹⁴, directly from the non-isothermal crystallization data obtained by DSC. In most cases, the results obtained through this method are considered good. The literature contains reports of unsatisfactory results related to nonlinear regression; however, these unsatisfactory results are more likely to be justified by the limitations of the model of crystallization kinetics in describing the non-isothermal crystallization of the polymer than by the nonlinear regression method itself^{13,15}.

One advantage of nonlinear regression is that it requires less work than the master curve approach. However, in order to perform nonlinear regression, which is usually based on the Leven-Marquardt^{12,13} method, sophisticated software is indispensable. The master curve approach has the advantage that it can be applied through any electronic spreadsheet. These two methods are usually employed after previous correction of the temperature lag between the DSC oven and the polymeric sample; in this aspect, they are both equally work-intensive.

The master curve approach requires the kinetic crystallization model to be in the form of Equation 1¹¹. Other equations, such as Malkin's^{1,16}, also fit this model; however, the method is applied

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almost exclusively to the Nakamura equation, mostly in Isayev's various scientific works⁶⁻⁹. In this respect, nonlinear regression is more flexible; moreover, it can be applied to other types of equation, not only to those that fit into the form of Equation 1. Nonlinear regression is being used by different researchers in various research groups¹¹⁻¹⁵. Difficulty in identifying the temperature at the beginning of the crystallization process is inherent to DSC experiments; thus, it occurs in both methods^{2,17}.

In the analysis and manipulation of the data to apply the Master Curve Approach, the present authors²⁻⁵ found that one of the main problems was the difficulty in determining the experimental induction time, which is a problem inherent to DSC analysis. It would be very useful to have experimental crystallization data for a polymer sample that: a) is perfectly described by a kinetics model such as the Nakamura equation; b) whose exact non-isothermal rate constant and corresponding induction time are known; and c) whose temperature lag between the DSC furnace and the sample are known exactly. In this case, some kind of validation could be made of the available procedures for calculating the kinetic parameters. Unfortunately, these ideal conditions do not exist.

Therefore, this work presents a methodology that can meet the aforementioned ideal conditions. To this end, *pseudo-experimental* non-isothermal crystallization curves were generated at different cooling rates using the Nakamura Model¹⁰. Thus, for these *pseudo-experimental* curves, any problem in the Master Curve Approach must be attributed to errors in the process of calculating the kinetic parameters. By using the *pseudo-experimental* curves, it is possible to know how close the retrieved parameters are from the parameters used to build the *pseudo-experimental* curves.

To minimize the influence that previous knowledge of the kinetic parameters used to generate the *pseudo-experimental* curves would have exerted, the author who applied the Master Curve Approach did not receive previous information about the kinetic parameters of the *pseudo-experimental* data generated by the other author. Thus, a blind analysis was performed. This procedure will be made clearer in the Methodology section.

1.1. Theoretical background

The fundamentals of the Master Curve Approach are well described in the paper of Isayev et al.¹ and will be mentioned only briefly herein. The Master Curve Approach is based only on experimental crystallization data and on the validity of the following general equation to express the crystallization kinetics:

$$\frac{d\theta}{dt} = K(T)f(\theta) \quad (1)$$

where θ is the degree of crystallinity, T the temperature and t the time. Equation 1 assumes that the crystallization rate is a product of two functions: $K(T)$, which depends only on temperature, and $f(\theta)$, which depends only on the degree of crystallinity. Hence, if there are non-isothermal crystallization data at different cooling rates for a given constant degree of crystallinity in each cooling condition, a shift factor for the non-isothermal crystallization rate constant can be defined according to Equation 2:

$$\frac{\left(\frac{d\theta}{dt}\right)_{ij}}{\left(\frac{d\theta}{dt}\right)_{rj}} = \frac{K(T_{ij})f(\theta_j)}{K(T_{rj})f(\theta_j)} = \frac{K(T_{ij})}{K(T_{rj})} = a_T(T_{ij}) \quad (2)$$

where $a_T(T_{ij})$ is the shift factor at temperature T_{ij} with reference to temperature T_{rj} . The symbol i denotes the i -th cooling rate and j denotes the j -th constant degree of crystallinity at which the shift factor

$a_T(T_{ij})$ is being calculated. So, for a constant degree of crystallinity j at each cooling rate (for example $\theta = 0.1$), the shift factor $a_T(T_{ij})$ relates to the non-isothermal rate constant at the corresponding temperatures at which $\theta = 0.1$ is reached. T_{rj} is the temperature at which $\theta = 0.1$ for the cooling rate taken as reference. For example, if $10^\circ\text{C}/\text{min}$ is chosen as the reference cooling condition, for $\theta = 0.1$ T_{rj} will be equal to $T_{10^\circ\text{C}/\text{min}; \theta = 0.1}$, and $K(T_{rj}) = K(T_{10^\circ\text{C}/\text{min}; \theta = 0.1})$ will be the denominator in Equation 2 for this degree of crystallinity. Obviously, the shift factor $a_T(T_{ij})$ will be equal to one for $10^\circ\text{C}/\text{min}$, because this is the reference condition. However, each i -th degree of crystallinity will have its own reference temperature T_{rj} , as for example, for $\theta = 0.5$, $T_{rj} = T_{10^\circ\text{C}/\text{min}; \theta = 0.5}$. If a temperature T_r is chosen among the T_{rj} temperatures as the overall reference temperature (e.g., $T_r = T_{10^\circ\text{C}/\text{min}; \theta = 0.1}$), the plots of $a_T(T_{ij})$ vs. T_{ij} at a constant degree of crystallinity, j , can be shifted to obtain a single plot of the shift factor as a function of temperature, $a_T(T)$ vs. T .

From the $a_T(T)$ vs. T curve, Isayev et al.¹ defined the reduced time for non-isothermal crystallization, ξ , with respect to the reference temperature, T_r , as follows:

$$\xi = \int_0^t a_T(T(t')) dt \quad (3)$$

where

$$a_T(T) = \frac{K(T)}{K(T_r)} \quad (4)$$

The θ vs. ξ curves for the different cooling rates should fall on an isothermal master curve at the general reference temperature T_r . This means that the reduced time transforms the non-isothermal crystallization data into isothermal crystallization data at this reference temperature. Thus, the half-time of crystallization ($t_{1/2, T_r}$ at the reference temperature can be evaluated from the isothermal master curve.

The non-isothermal crystallization rate constant at the reference temperature is therefore obtained from the following equation:

$$K(T_r) = \frac{1}{(t_{1/2, T_r})^n} \quad (5)$$

where n is the Avrami index, which is 3 in this case. From $K(T_r)$ and Equation 4, $K(T)$ can be calculated for the whole range of temperatures in which the shift factor a_T vs. T was calculated. The $K(T)$ vs. T data can then be fitted by the Hoffman & Lauritzen equation¹⁸:

$$K(T) = (\ln 2)^{\frac{1}{n}} \left(\frac{1}{t_{1/2, T_r}} \right)_0 \exp\left(\frac{-U/R}{T - T_\infty} \right) \exp\left(\frac{-K_g}{T\Delta T f} \right) \quad (6)$$

where $(1/t_{1/2, T_r})_0$ is a pre-exponential factor that includes all terms independent of temperature; U is the activation energy for the transport of crystallizing units across the phase boundary; K_g is the nucleation exponent; $T_\infty = T_g - 30\text{ K}$ is the temperature below which molecular transport ceases; R is the universal gas constant; $\Delta T = T_m^0 - T$ is the degree of supercooling, $f = 2T / (T_m^0 + T)$ is a correction factor accounting for the reduction in the latent heat of fusion as the temperature is decreased, and T_m^0 is the equilibrium melting temperature.

Using the calculated $K(T)$ and assuming n equal to 3, the differential form of the Nakamura equation¹⁰, given by Equation 7, can be used to simulate the $d\theta/dt$ vs. T curves, which are integrated to obtain

the θ vs. T curves. These simulated data can then be compared with the experimental ones to check the quality of the kinetic parameters calculated by the Master Curve Approach.

$$\frac{d\theta}{dt} = nK(T)(1-\theta)[- \ln(1-\theta)]^{n-\frac{1}{n}} \quad (7)$$

1.2. Methodology

As mentioned before, *pseudo-experimental* calorimetric data were generated by the Nakamura Model, given by Equation 7, using typical parameters reported in the literature. Through this procedure, it is possible to have a very clear idea of how close the retrieved kinetic parameters calculated by the Master Curve Approach are from the original values. The following parameters for polypropylene¹⁹ were used in association with the Nakamura Model to generate the *pseudo-experimental* data:

$U^* = 1500$ cal/mol;
(Activation energy for molecular transport)

T_g (Polypropylene) = -18 °C;
(Glass transition temperature)

$T_m^0 = 172$ °C;
(Equilibrium melting temperature)

$(1/t_{1/2})_0 = 54,95e7$ s⁻¹;
(Pre-exponential factor that includes all terms independent of temperature in the Hoffman & Lauritzen equation)

$K_g = 3,99$ e5 K²;
(Nucleation constant)

$\Delta H_c = -100$ J.g⁻¹;
(Latent heat of crystallization ΔH_c)

mass = 10 mg;
(Sample mass)

The Nakamura equation does not take into account the induction time for the onset of crystallization. However, this parameter is necessary to generate the *pseudo-experimental* data for applying the Master Curve Approach. This non-isothermal induction time was therefore estimated using the Godovsky and Slonimsky equation²⁰:

$$t_{in} = \left[\frac{t_m(a+1)}{b^a} \right]^{\frac{1}{a+1}} \quad (8)$$

where b is the constant cooling rate; and a and t_m are material constants independent of temperature.

In a DSC curve, the non-isothermal induction time is calculated by Equation 9:

$$t_{in} = \frac{T_m^0 - T_{ic}}{b} \quad (9)$$

Thus, the initial crystallization temperature that was used in association with the Nakamura equation to generate the *pseudo-experimental* data was obtained by the following equation:

$$T_{ic} = T_m^0 - bt \quad (10)$$

The following parameters were used to estimate the induction time¹⁹: $a = 10$ and $t_m = 5.99e18$ sK¹¹. From this point forward, when comparing any retrieved kinetic parameters with original values

employed to generate the *pseudo-experimental* calorimetric curves, the original values will be referred to as the “true parameters”.

An additional difficulty was incorporated to the *pseudo-experimental* data simulated by the Nakamura equation. In this case, the values for the simulated heat flow vs. temperature curves for each cooling rate were added to the respective experimental baseline of a Perkin-Elmer DSC7. Thus, baseline noises caused some imprecision when attributing the temperature corresponding to the beginning of the crystallization process. The *pseudo-experimental* data represented by heat flow vs. temperature curves were generated by the following expression:

$$\dot{Q} = m \cdot \Delta H_c \frac{d\theta}{dt} \quad (11)$$

where \dot{Q} and $\frac{\dot{Q}}{m}$ are the heat flux in mW and W/g, respectively.

In summary, the following steps were carried out to generate the *pseudo-experimental* data:

- Calculation of the induction time t_{in} and the temperature at the onset of crystallization, T_{ic} , for each cooling rate, using Equations 8 and 10, respectively;
- Calculation of the crystallization rate, $d\theta/dt$, as a function of temperature, using Nakamura equation given by Equation 7, using the parameters reported in the literature;
- Calculation of the heat flow curve in mW as a function of temperature, based on Equation 11; and
- Addition of the curve calculated in c to an actual DSC baseline for its respective cooling rate, thereby obtaining the *pseudo-experimental* curves shown in Figure 1.

Figure 1 shows the *pseudo-experimental* data after the baseline addition for all the cooling rates used in the present work. These curves correspond to the data sent to the author who applied the Master Curve Approach to retrieve the non-isothermal crystallization rate constant. It is important to point out again that the only information given to this author were the following parameters: $U^* = 1500$ cal/mol; T_g (PP) = -18 °C; $T_m^0 = 172$ °C and $m = 10$ mg. A blind analysis was performed to avoid influencing the results. Thus, the applicability of the method was tested for data described perfectly by the Nakamura Model and parameters known absolutely by only one of the authors. This procedure enabled us to identify exactly what errors could occur in the analysis.

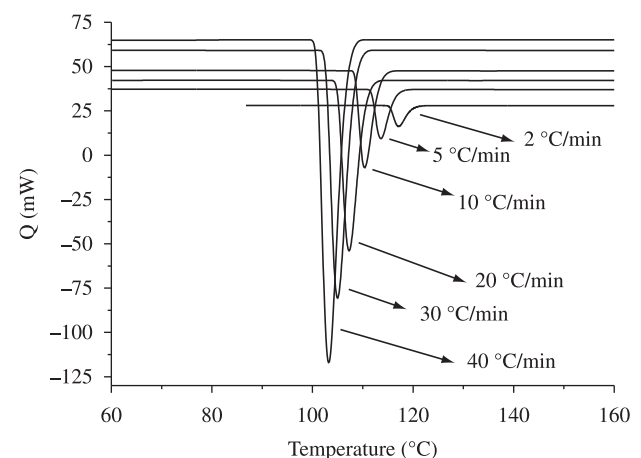


Figure 1. Pseudo-experimental data after baseline addition for all cooling rates used in the present work.

The author who analyzed the Master Curve Approach saw the *pseudo-experimental* data as *experimental* non-isothermal curves obtained for a polymer sample in a DSC. The normal procedure for obtaining the non-isothermal crystallization rate constant was therefore applied using these *pseudo-experimental* data. Thus, it was necessary to define the temperature of the onset of crystallization (obviously without knowing the *true* value) for each cooling rate. The θ vs. Temperature curve was thus determined (as well as the corresponding θ vs. time curve for each cooling rate) by applying the method of partial area calculation. Its derivative curve $d\theta/dt$ vs. Temperature was thus obtained and the Master Curve Approach was applied to calculate the “*unknown*” non-isothermal crystallization rate constant that describes the *pseudo-experimental* data.

2. Results and Discussion

Figure 2 shows the plots of the crystallization rate as a function of sample temperature. As expected, higher cooling rates led to larger and broader peaks and lower onset and peak temperatures, as well as higher crystallization rates. The curves in Figure 2 were used in association with Equation 2 to calculate the $a_T(T_{ij})$ vs. T_{ij} for several constant degrees of crystallinity j , resulting in the curves shown in Figure 3. Thus, the general reference temperature $T_r = 111.09$ °C was chosen, and the curves of Figure 3 were shifted to obtain the master curve for the shift factor. As can be seen in Figure 4, an excellent superposition of the kinetic data was obtained, even for degrees of crystallinity as low as $\theta = 0.01$ and $\theta = 0.05$. When the Master Curve Approach is applied to experimental data, deviations are usually observed for such low degrees of crystallinity.

Using the shift factor, the reduced time ξ was evaluated for each cooling rate based on Equation 3. Figure 5 shows that a highly defined master curve was obtained for θ vs. time at the reference temperature, $T_r = 111.09$ °C. The parameter $(t_{1/2})_{T_r}$ was obtained from the master curve θ vs. ξ , and $K(T_r)$ was then calculated using Equation 5. Thus, $K(T)$ could be determined as a function of temperature by Equation 4. These values of $K(T)$ were then fitted by Equation 6. In this way, the kinetic parameters $(1/t_{1/2})_0$ and K_g were retrieved.

The retrieved non-isothermal crystallization rate constant was used, in association with the Nakamura Model, to build the plots of the relative crystallinity θ as a function of temperature at the various cooling rates. Figure 6 shows an excellent agreement between the *pseudo-experimental* curves and the simulated curves based on the retrieved parameters. Therefore, it was concluded that the Master

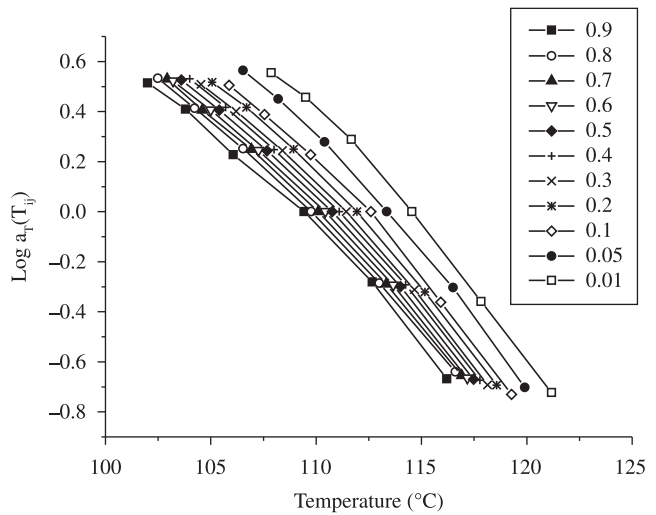


Figure 3. $a_T(T_{ij})$ vs. T_{ij} for several constant degrees of crystallinity j .

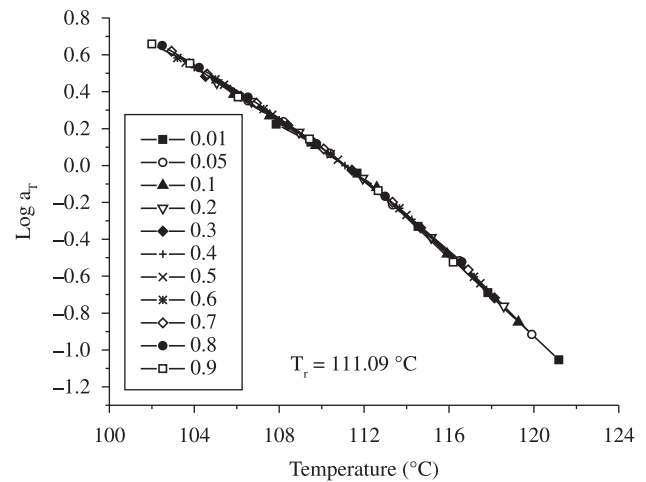


Figure 4. Master curve for the shift factor for the non-isothermal crystallization rate constant as a function of temperature.

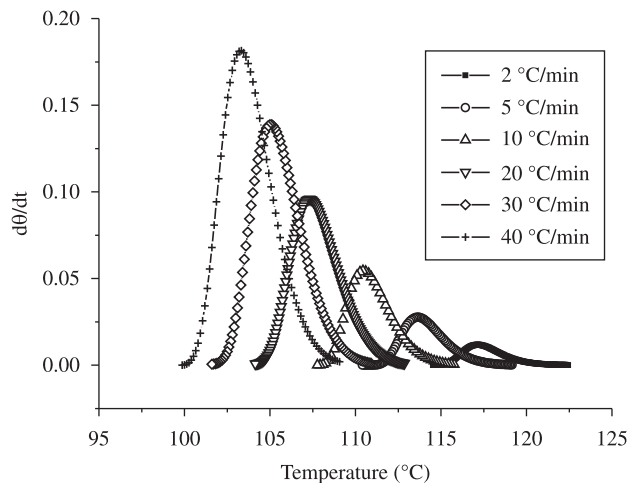


Figure 2. Crystallization rate as a function of sample temperature.

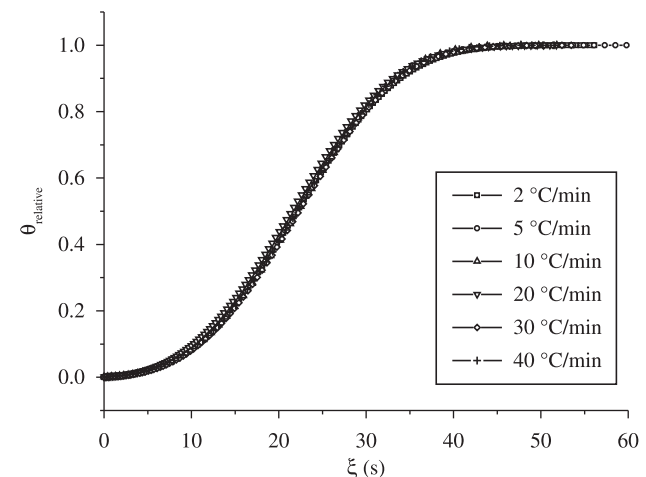


Figure 5. Master Curve of θ as a function of reduced time for isothermal crystallization at the reference temperature $T_r = 111.09$ °C.

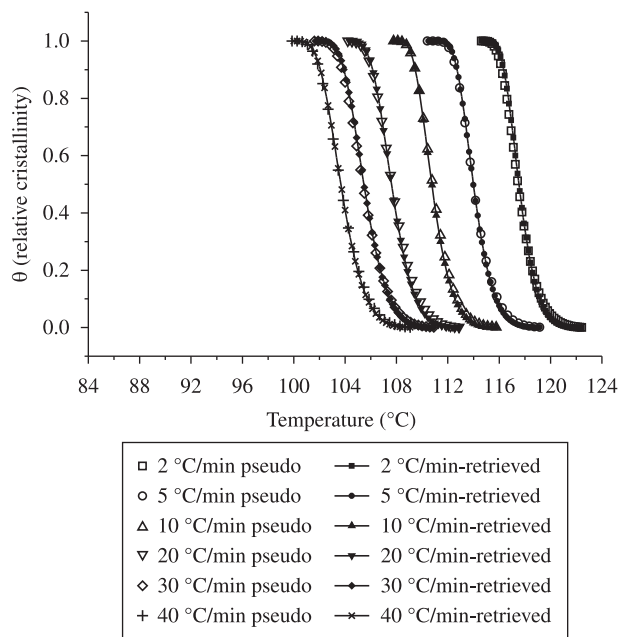


Figure 6. Plots of relative crystallinity θ as a function of temperature generated by the Nakamura Model using the *true* and retrieved $(1/t_{1/2})_0$ and K_g values.

Curve Approach allowed for the determination of the non-isothermal crystallization rate constant of the Nakamura equation with very high accuracy. It was also concluded that the noises in the baseline did not affect the definition of the induction time (temperature of the onset of crystallization). A third conclusion that should be noted is that the problems in reproducing actual non-isothermal experimental data of polymers by the Nakamura equation using parameters obtained by the Master Curve Approach result from the fact that this model does not provide a perfect description of crystallization kinetics.

If the *pseudo-experimental* curves in Figure 6 were actual experimental data, the analysis would be concluded. It can also be assumed that the kinetic parameters calculated by the Master Curve Approach are very close to the *true* values because an almost perfect reproduction of the *pseudo-experimental* data was obtained. However, due to the methodology employed here, this analysis could be taken further to answer the question of how close the retrieved kinetic parameters are from the *true* values. As mentioned earlier, one of the authors knew the exact *true* induction times and the *true* kinetic parameters which were used to build the *pseudo-experimental* curves. Therefore, it is possible to determine if errors occurred in the *blind* analysis performed by the other author.

The initial point of the Master Curve Approach is the attribution of the temperature corresponding to the onset of crystallization, Tic, in the DSC curves. Figure 7 shows the Tic values assigned to some cooling rates and the *true* values initially used to build the *pseudo-experimental* curves.

As can be seen, the Tic values are approximately 2 °C lower than the *true* values. Table 1 presents this comparison for all the cooling rates. It also shows the heat of crystallization retrieved from the Master Curve Approach by integrating the partial area between the DSC curve and its baseline. Note that the maximum error obtained in this parameter is negligible, i.e., about 1% for a cooling rate of 30 °C/min.

The criterion used in attributing values to the temperature corresponding to the onset of crystallization is the deviation of DSC trace from its baseline. This deviation corresponds to a minimum heat release that can be detected by the DSC and that can be distinguished from the noises in the baseline. However, Figure 7 indicates that, at the *true*

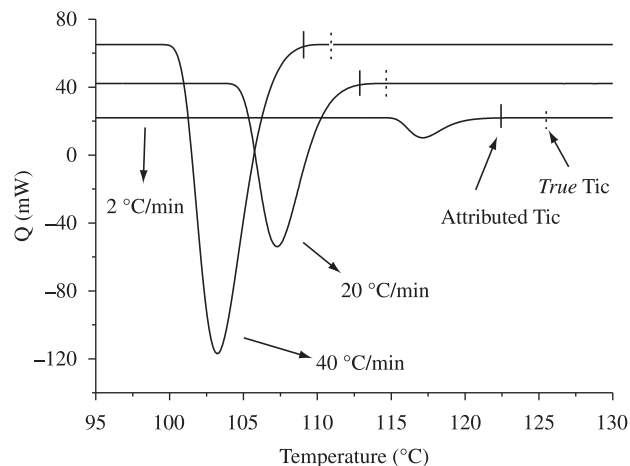


Figure 7. Attributed Tic values for some cooling rates and *true* values initially used in the generation of the pseudo-experimental curves.

Table 1. *True* and retrieved Tic and ΔH_c values.

Cooling rate	<i>True</i> Tic (°C)	Retrieved Tic (°C)	<i>True</i> ΔH_c (J.g ⁻¹)	Retrieved ΔH_c (J.g ⁻¹)
(2 °C/min)	125.50	122.44	-100	-100.2
(5 °C/min)	121.46	119.17	-100	-100.1
(10 °C/min)	118.18	115.77	-100	-100.1
(20 °C/min)	114.68	112.87	-100	-100.7
(30 °C/min)	112.52	110.9	-100	-101.0
(40 °C/min)	110.95	109.07	-100	-100.3

Tic value, the crystallization rate predicted by the Nakamura Model in Equation 11 is extremely slow in the initial stages of crystallization. Therefore, the corresponding heat release is insufficient to cause a visible deviation from the baseline. For the author who applied the Master Curve Approach, at the *true* Tic value in the heat flux vs. temperature curve, there was no evidence that crystallization had begun, so any attempt to attribute a Tic value close to the *true* temperature would be mere speculation. Therefore, although the retrieved Tic values are not the *true* ones, they are more plausible because they represent the starting point of a visible deviation from the baselines.

It is now interesting to ascertain if this difference between the *true* Tic values and the retrieved ones influence the kinetic parameters K_g and $(1/t_{1/2})_0$ in any way. Table 2 presents a comparison between the *true* K_g value and $(1/t_{1/2})_0$ and the corresponding parameters calculated by the Master Curve Approach. This table also compares the retrieved a and t_m parameters obtained through the Godovsky and Slonimsky equation using the attributed Tic value and the *true* ones. As expected, the difference in Tic values leads to differences in the parameters a and t_m of the induction time model given by Equation 8.

Table 2 indicates that the calculated K_g is almost identical to the *true* value. However, the retrieved $(1/t_{1/2})_0$ is about 4% lower than the *true* one. Figure 8 shows the non-isothermal rate constant $K(T)$ calculated by Equation 6 for the two sets of parameters. Apparently, the difference between the *true* $K(T)$ and the retrieved $K(T)$ is not significant. Therefore, it does not explain why the use of different Tic values did not insert errors in the replication of the *true* θ vs. T curves, as shown in Figure 6.

To understand the influence of different Tic values and the various parameters of the Nakamura Model on the θ vs. T curves, Figure 9 presents simulated data using a variety of combinations of *true* and

Table 2. True and retrieved $(1/t_{1/2})_0$ and K_g values of the non-isothermal crystallization rate constant of the Nakamura Model and true and retrieved values of the Godovsky and Sloninsky equation of the induction time.

Parameter	True value	Retrieved value
$(1/t_{1/2})_0$	$54.95e7 \text{ s}^{-1}$	$52.72e7 \text{ s}^{-1}$
K_g	$3.990 \text{ e}5 \text{ K}^2$	$3.996e5 \text{ K}^2$
a	10	11.59
t_m	$5.99e + 18 \text{ sK}^{10}$	$4.99e + 21 \text{ s.K}^{11.59}$

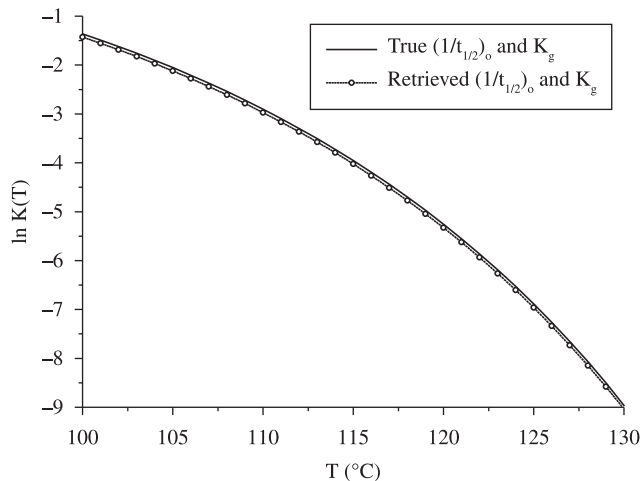


Figure 8. Non-isothermal rate constant $K(T)$ calculated by Equation 6 for true and retrieved set of parameters $(1/t_{1/2})_0$ and K_g .

retrieved parameters for the cooling rate of $20 \text{ }^\circ\text{C}/\text{min}$. Note that when the same Tic is used, the crystallization kinetics predicted by the true $(1/t_{1/2})_0$ and K_g is faster than the one predicted based on the retrieved parameters. This was expected, because true $(1/t_{1/2})_0$ is 4% higher than the one calculated by the Master Curve Approach. Note, also, that when the same set of parameters $(1/t_{1/2})_0$ and K_g is used, the θ vs. T curves calculated by the true Tic value are higher than the ones calculated with the retrieved Tic. This was expected, since the Tic value attributed by the author who applied the Master Curve Approach was approximately $2 \text{ }^\circ\text{C}$ lower than the true one, as shown in Figure 7 and Table 1.

Another comparison that can be made in Figure 9 is between the curves predicted by the true set of parameters (Tic, $(1/t_{1/2})_0$ and K_g) and the retrieved set of parameters. As can be seen, there is a very significant difference. In this case, the crystallization predicted by the true parameters begins and ends much earlier than that predicted by the retrieved parameters.

However, this latter result seems inconsistent compared with the result presented in Figure 6, which shows an excellent agreement between the pseudo-experimental data and the predicted curves (simulated with the retrieved parameters). After a detailed analysis, it was found that the reason for the difference between Figures 6 and 9 is a peculiarity of the differential form of the Nakamura Model. Equation 7 shows that for θ equal to zero, the rate of crystallization $d\theta/dt$ is zero. Therefore, according to the numerical procedure for calculating the progress of the crystallization process, a negligible $\theta_{t=0}$ must be used in Equation 12, albeit different from zero. Otherwise, $(d\theta/dt)_{t=0}$ will be zero and $\theta_{t+\Delta t}$ will always be zero.

$$\theta_{t+\Delta t} = \theta_t + \left(\frac{d\theta}{dt} \right)_t \Delta t \quad (12)$$

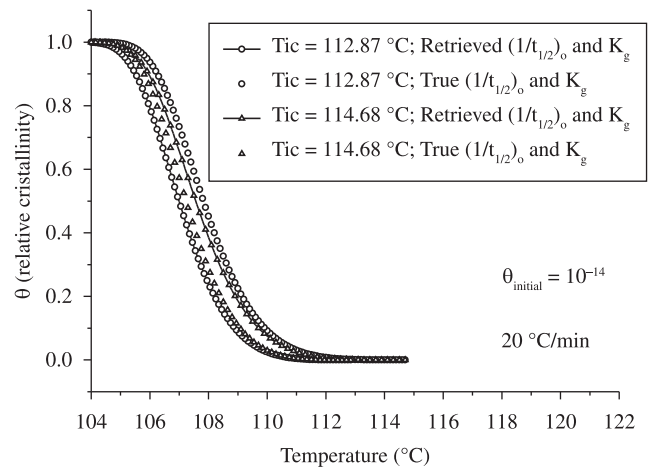


Figure 9. Influence of different Tic values and different $(1/t_{1/2})_0$ and K_g values of the non-isothermal rate constant on θ vs. T curve for the cooling rate of $20 \text{ }^\circ\text{C}/\text{min}$.

However, because a blind analysis was carried out, the author who applied the Master Curve Approach assumed $\theta_{t=0} = 10^{-3}$, while the condition used in the generation of the pseudo-experimental data was $\theta_{t=0} = 10^{-14}$, as proposed by Isayev and Catignani¹⁹.

As mentioned earlier, the Nakamura Model presents an extremely slow initial crystallization rate. Thus, in the initial stages of crystallization, it takes a considerable amount of time to go from $\theta = 10^{-14}$ to $\theta = 10^{-3}$. To show this significant effect, Figure 10 presents the curves of θ vs. T for these two initial θ , but using only the retrieved set of parameters Tic, $(1/t_{1/2})_0$ and K_g determined by the author who applied the Master Curve Approach. As can be seen, the use of $\theta_{\text{initial}} = 10^{-3}$ causes a considerable shift of the θ vs. T curve to higher temperatures compared with the corresponding θ vs. T curve calculated by $\theta_{\text{initial}} = 10^{-14}$.

Therefore, the discrepancy between the data in Figures 6 and 9 can be explained based on the fact that, in the former, the retrieved set of parameters Tic, $(1/t_{1/2})_0$ and K_g were used with θ_{initial} equal to 10^{-3} , while in the latter, the true set of parameters was used with θ_{initial} equal to 10^{-14} .

However, in Figure 9 the two sets of parameters were compared using only θ_{initial} equal to 10^{-14} . Thus, the difference in θ_{initial} compensated for the difference in other parameters, allowing for the excellent congruence between the pseudo-experimental data and the retrieved data shown in Figure 6. In Figure 9, due to the use of the same $\theta_{\text{initial}} = 10^{-14}$, the difference between the curves obtained by the true and retrieved set of parameters $(1/t_{1/2})_0$, K_g and Tic is clearly visible.

Figure 11 presents the heat flow vs. temperature curves generated with different θ_{initial} . Note that there is a significant difference between the true heat flow curve (pseudo-experimental data) and the curve generated using $\theta_{\text{initial}} = 10^{-14}$ with the retrieved set of parameters Tic, $(1/t_{1/2})_0$ and K_g . However, if the retrieved set of parameters is used with $\theta_{\text{initial}} = 10^{-3}$, the heat flow curve shifts toward the pseudo-experimental data.

For technological purposes, the description of the crystallization process given by the retrieved values suffices for the simulation of polymer processing. As Figure 6 indicates, the retrieving process allowed for a very good description of the true crystallization kinetics. Hence, the crystallinity, the heat release and its influence on the temperature profile would be correctly predicted using this retrieved set of parameters. In this case, the use of θ_{initial} equal to 10^{-3} is very convenient because it can be used with a Tic that is much easier to define than the true one. As shown in Figure 7, trying to define Tic

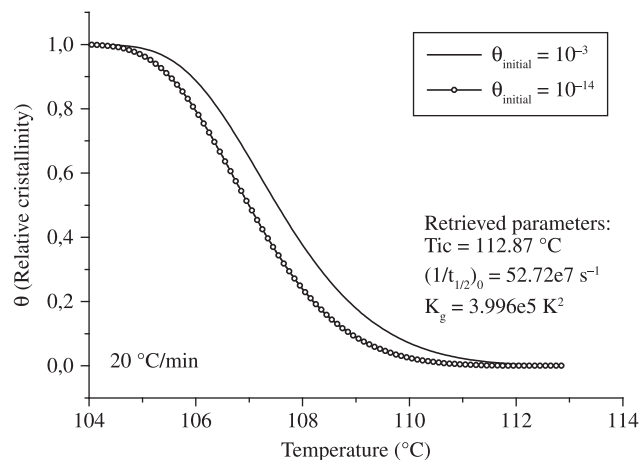


Figure 10. θ vs. T curves for two different initial degrees of crystallinity, but using only the retrieved set of parameters T_{ic} , $(1/t_{1/2})_0$ and K_g .

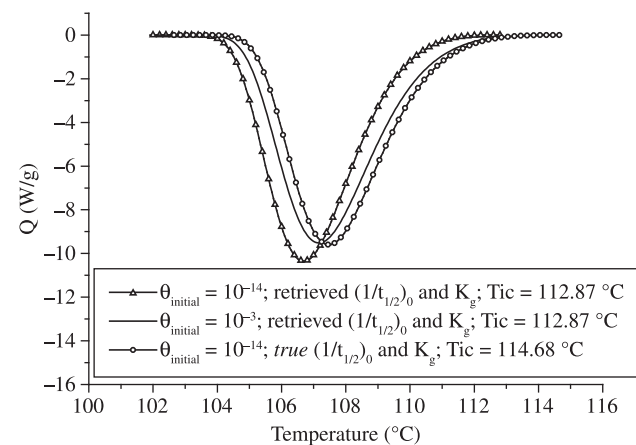


Figure 11. Influence of $\theta_{initial}$ on the heat flow vs. temperature curves.

at the *true* position would be mere speculation, since there is no evidence of any deviation from the baseline.

3. Conclusions

As expected, the Master Curve Approach proved to be completely compatible with non-isothermal crystallization data perfectly described by the Nakamura Model. The imprecision in the determination of the temperature corresponding to the onset of crystallization caused no problems in the description of the *pseudo-experimental* crystallization data. However, this congruence was possible due to a compensation effect, since there were some differences between the *true* and retrieved set of parameters $(1/t_{1/2})_0$, T_{ic} and $\theta_{initial}$. These problems were not caused by the Master Curve Approach, but by difficulties inherent to the DSC analysis. The use of $\theta_{initial}$ equal to 10^{-3} for the differential form of the Nakamura Model proved to be more convenient than 10^{-14} , because it allowed for the use of a more easily defined T_{ic} .

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