

## Some issues on polymer crystallization kinetics studied by DSC non isothermal tests

Gaetano Lamberti(✉) and Carlo Naddeo

Department of Chemical and Food Engineering, University of Salerno, Via Ponte don Melillo, 84084 Fisciano (SA), Italy

Fax: +39 089964057; e-mail: glamberti@unisa.it

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### Summary

In this work constant cooling rate crystallization experiments were carried out by a DSC, working with an iPP and using a very little amount of material, to minimize the heat transfer resistance in the mass of the sample. The resulting data were corrected to take into account also for the external heat transfer resistance. The corrected data were compared with data produced in the past, working with larger amounts of the same resin in a less accurate DSC apparatus, confirming that in the field of polymer crystallization kinetics the calorimeter has to be used carefully. The data were also used to check a kinetic model previously tuned under isothermal conditions. Up to 10°C/min (0.167 K/s) the isothermal model is accurate enough, but faster tests requires an improvement of the model.

### 1. Introduction

Almost all the polymer transformation processes involve a cooling step that causes the polymer solidification. During the solidification, the semi-crystalline polymers can develop structures partially ordered, often typified by three-dimensional objects known as spherulites. In turn, the crystallinity affects the final object properties. Therefore, detailed knowledge of crystallization kinetics is highly desirable to manage polymer transformation processes.

Traditionally the most of experimental work in polymer crystallization kinetics research was done by differential scanning calorimetry (DSC). This technique is based on measurements of heat released (or required) by a polymeric sample during its solidification (or its melting). Enthalpy released (or required) can be related to the phase transitions that take place in the sample. Tests can be carried out under isothermal conditions with a limited degree of under-cooling or under constant cooling rates up to about 1 K·s<sup>-1</sup> (60°C/min). Subsequently, the crystallinity evolutions drawn from DSC measurements were adopted as source of data for validation of crystallization kinetic models. However, it has been theoretically predicted [1] that the common use of the DSC apparatus, which recommend to operate with large samples in the pan (up to tens of mg), can cause the wrong determination of kinetics, and thus the incorrect tuning of the kinetic model.

Aims of this work are to investigate the impact of using limited amount of sample in DSC measurements on kinetics studies, and to check the capability of a kinetic model, tuned under isothermal conditions [2], in prediction of non isothermal kinetics.

## 2. Experimental

Along this work a commercial iPP supplied by Montell (T30G,  $M_w = 481000$ ,  $M_n = 75000$ , tacticity = 87.6%*mmmm*) has been used. We adopted a commercial iPP since this study is a part of a larger investigation, devoted to clarify the crystallization kinetics of commercial resins under processing conditions.

Non-isothermal crystallization tests were carried out using a Thermal Analyzer Mettler Toledo mod. 822/400 equipped with DSC cell purged with nitrogen and chilled with liquid nitrogen for sub-ambient measurements. The samples were heated up to 240°C, kept at this temperature for 30 min to assure the complete melting of any structure, and then cooled to 0°C at the desired cooling rate. Alfonso and Ziabicki [3] have demonstrated the importance of erasing the previous thermo-mechanical history during studies of crystallization kinetics. Working with iPP, they suggest to keep the polymer at high temperature (more than 230°C) for large period of time (more than 30 min). These conditions were found to be not the cause for material degradation. In the present work, a further confirmation of this fact was found, since the same sample was used for repeated tests, giving the same response. Nine different tests were performed, at cooling rate of {2.5, 5, 10, 15, 20, 25, 30, 40, 50 °C/min}.

To minimize the effects due to heat transfer phenomena [1], very little amount of material has been used (2.3 mg). Two layers of a 60µm film, shaped as 5 mm diameter disks, were placed in the DSC pan. In principle, the use of only one film can improve the accuracy of the measurements. However, the polymer was melt and kept at high temperature for enough time to ensure the full disappearing of previous history also in term of shape (i.e. one or two layer). The data, as collected from the DSC, are reported in Figure 1 in term of DSC signal (for mass unit) versus the furnace temperature. The cooling rate investigated can cause the formation of only alpha-phase spherulites, Lamberti and Brucato [4]. Furthermore, the final level of crystallinity is almost insensitive to the cooling rate. Thus, the amount and the morphology of developed crystallinity does not affect the measurements.

## 3. Model equations

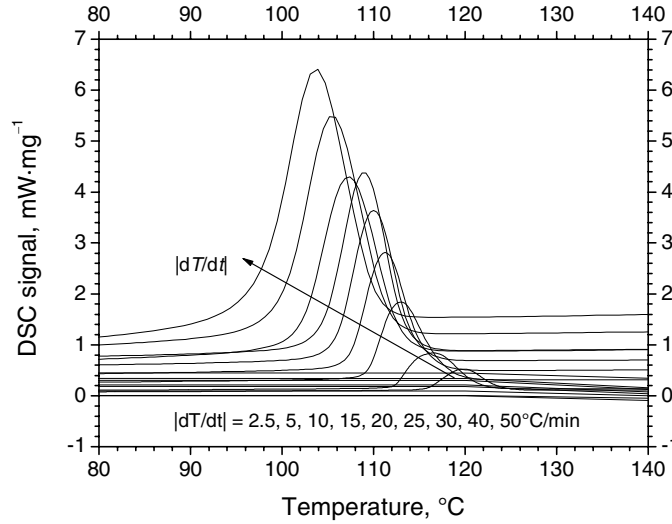
Subjects of this section are to summarize the equations of the crystallization kinetics model proposed by [2] (§ 3.1), and to summarize the method suggested by [5] to correct the DSC signal (§ 3.2).

### 3.1 Summary of the crystallization kinetics modeling

In a previous work [2] the kinetics of *degree of space filling*,  $\xi_g$ , for the iPP used along this work has been described on the basis of the well-known Kolmogoroff-Avrami-Evans equation (KAE equation) [6-8]:

$$\xi_g(t) = 1 - \exp[-E(t)] \quad (1)$$

Where  $E(t)$  is the *expectancy* of the crystalline phase, i.e. the volume that the crystals would occupy if no impingement occurs.



**Figure 1** – Raw data of calorimetric signal,  $\text{mW}\cdot\text{mg}^{-1}$ , versus temperature,  $^{\circ}\text{C}$ , as obtained from the DSC, for all the cooling rates investigated.

In the model, the expectancy was calculated on the basis of the nucleation phenomenon, described by the nuclei density  $N$ , followed by three-dimensional isotropic growth, described by the growth rate  $G$ :

$$E(t) = \frac{4\pi}{3} \int_0^t \left[ \frac{dN}{dT} \frac{dT}{d\theta} \right] \left[ \int_0^t G(\tau) d\tau \right]^3 d\theta \quad (2)$$

Growth rate has been expressed on the basis of the Lauritzen-Hoffmann theory [9]:

$$G = G_0 \exp \left[ -\frac{U^*}{R(T - T_g + T_{\infty})} \right] \exp \left[ -\frac{\kappa_G (T_m)^2 (T_m + T)}{2T^2 (T_m - T)} \right] \quad (3)$$

Nuclei density has been obtained from the isothermal tests [2]:

$$N = N_0 \exp \left[ -3 \frac{(\kappa_t - \kappa_G) T_m^2 (T_m + T)}{2T^2 (T_m - T)} \right] \quad (4)$$

All the values for the parameters in equations (2-4) have been tuned in [2] and they are summarized in Table 1.

**Table 1** - Parameter values for modelling the quiescent non-isothermal crystallization kinetics.

$T_m$	$T_g^0$	$T_{\infty}$	$U^*/R$	$G_0$
K	K	K	K	m/s
467.15	263.15	51.6	2068.8	$4.36 \cdot 10^8$
$\kappa_G$	$N_0$	$\kappa_t$	$\alpha$	$\beta$
dimensionless	nuclei/ $\text{m}^3$	dimensionless	$(\text{K/s})^{-\beta}$	dimensionless
2.7979	$1.52 \cdot 10^{16}$	3.1710	4.0	1.5

### 3.2 Summary of the corrections proposed by Eder *et al.*, 1997 [5]

Traditionally, the crystallinity evolution with temperature was obtained from the DSC cooling ramps, after baseline subtraction, by resolution of the integral:

$$I(T) = \frac{1}{\dot{T}} \int_{T_0}^T \phi(\tau) d\tau \quad (5)$$

Where  $T_0$  is the starting temperature of the cooling (a temperature above the resin melting point),  $T$  is the actual temperature as indicated by the DSC apparatus,  $\phi(T)$  is the DSC signal (mW) and  $\dot{T}$  is the cooling rate.

However, Eder *et al.*, 1997 [5] have demonstrated that the heat transfer phenomena between sample and DSC pan can affect consistently the result of the analysis carried out on the basis of equation (5). They suggested a correction of the data, based on the heat balance on the system pan/sample, which allows to estimate the relative crystallinity in a more precise way:

$$\xi_g(T) = \frac{1}{m_s \Delta H} \left[ \frac{\phi(T)}{\alpha} + I(T) \right] \quad (6)$$

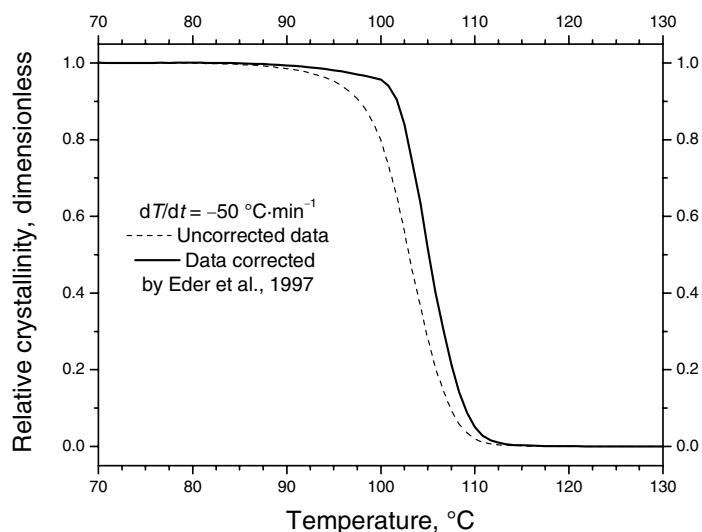
In equation (6)  $m_s$  is the sample mass,  $\Delta H$  is the heat of crystallization,  $\alpha$  is given by:

$$\alpha = \frac{\gamma}{m_s c_s + m_p c_p} \quad (7)$$

Where  $\gamma$  is an 'effective' heat transfer coefficient (it is actually given by the product of a 'traditional' heat transfer coefficient,  $h$ , for the transfer surface,  $A$ :  $\gamma = hA$ ,  $\text{mW}\cdot\text{K}^{-1}$ ),  $c_s$  and  $c_p$  are the specific heat of the sample and of the pan, and  $m_p$  is the pan mass. Furthermore, the sample temperature,  $T_s$ , does not follow instantaneously the furnace temperature read by the instrument,  $T$ , but it suffers of a delay that is function of cooling rate and of the heat transfer rate. The analysis of Eder *et al.*, 1997 [5] provided also an equation to estimate the sample temperature:

$$T_s = \frac{\phi(T)}{\gamma} + T - \frac{\dot{T}}{\alpha} \quad (8)$$

Where all the symbols are already known. The 'effective' heat transfer coefficient  $\gamma$  was evaluated from temperature relaxation after melting of indium, following the procedure suggested by Chan and Isayev [10]. A value of  $18.2 \text{ mW}\cdot\text{K}^{-1}$  was found. The corrections given by equations (6) and (8) were applied to all the tests. Figure 2 shows the evolution of relative crystallinity during the fastest cooling test ( $dT/dt = -50^\circ\text{C}\cdot\text{min}^{-1}$ ). The dashed line is the result of traditional analysis: signal integrated by equation (5) versus the furnace temperature (as read from the DSC apparatus), the continuous line is the result of the Eder *et al.* analysis: signal integrated by equation (6) versus the sample temperature given by equation (8). The real crystallization takes place at temperature higher than the one obtained by the analysis in which the heat transfer phenomena are neglected. The semi-crystallization temperature (the temperature correspondent to  $\xi_g = 0.5$ ) is about  $103^\circ\text{C}$  following the traditional analysis, and it is about  $105^\circ\text{C}$  following the analysis which takes in account for the heat transfer phenomena.



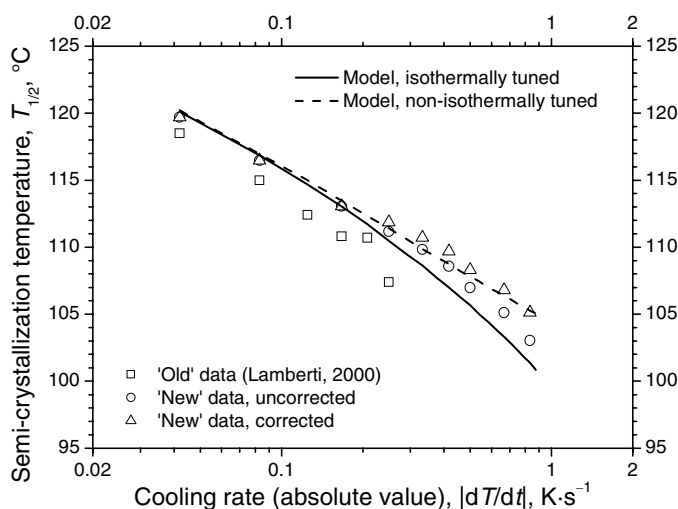
**Figure 2** – The relative crystallinity evolution during a cooling test ( $dT/dt = -50^{\circ}\text{C}\cdot\text{min}^{-1}$ ). Dashed line: DSC signal integrated and normalized after baseline subtraction versus temperature read from DSC (traditional analysis), continuous line: relative crystallinity versus sample temperature, both calculated accordingly with Eder *et al.*, 1997 [5].

#### 4. Results and discussions

The semi-crystallization temperature,  $T_{1/2}$ , i.e. the temperature at which the relative crystallinity is 0.5, can be used as a single value which localizes the temperature range correspondent to the crystallinity evolution (i.e., the crystallization takes place in a range “centred” around  $T_{1/2}$ ). In tuning of a model one has to consider a single number instead of an entire evolution: if the model predict nicely the semi-crystallization temperature, it will predict the full kinetics with sufficient precision. Semi-crystallization temperatures of the resin subject of this work are reported in Figure 3, versus the cooling rate experienced by the material during the test. The values have several sources, both experimental and modelling, which will be discussed in the following.

The same resin studied in the frame of this work has been already characterized in the past [11]; some cooling runs at constant rate were carried out by using a DSC. However, in that experiments large samples were used, following the specifications of DSC manufacturer, up to 10-15 mg. The semi-crystallization temperatures determined by this way are reported in Figure 3, as open squares. It is evident a decreasing trend (only the data at  $12.5^{\circ}\text{C}/\text{min} = 0.208^{\circ}\text{C}/\text{s}$  being out of the trend). The data set seems to be self-consistent, and follows the predicted trend (semi-crystallization temperature decreases with cooling rate). However, the use of large amount of material causes the development of large thermal gradients inside the samples. As a consequence, the exothermal DSC signal develops later, and the traditional analysis of the DSC signal predicts the crystallization to take place at temperature lower than the real ones [1]. Furthermore, the analysis were performed using a DSC apparatus which was not properly calibrated.

In Figure 3 are reported also the prediction of the model constituted by equations (1-4), tuned under isothermal conditions [2], as a continuous line. It is expected that, at least at lower cooling rates, the isothermal model will predict the experimental behaviour correctly. Instead, the model predicts the crystallization to takes place at temperature higher than the 'old' experimental values. Two explications are to be considered: i) the model, tuned under isothermal conditions, is not applicable in non-isothermal conditions, even if at lower cooling rates; ii) the data are not reliable. Due to the theoretical analysis carried out in [1], the second hypothesis seems to be the most realistic.



**Figure 3** – Semi-crystallization temperatures versus the (absolute value of) cooling rate. Open boxes (□) are data obtained in a previous work (on the same resin) [11], open circles (○) are uncorrected data obtained in the frame of this work, open triangles (△) are the same data, corrected accordingly to Eder *et al.*, 1997 [5]. The continuous line is the crystallization kinetic model, tuned under isothermal conditions [2], and the dashed line is the crystallization kinetic model, tuned under non-isothermal conditions [12].

The data obtained in this work, using very low amounts of material, are shown in Figure 3 as open circles. They are the uncorrected values, i.e. the semi-crystallization temperatures taken from the traditional analysis, simple drawing the result of the integral (5) versus the temperature as read from the DSC (the dashed line in Figure 2 is an example at  $50^{\circ}\text{C}/\text{min} = 0.833^{\circ}\text{C}/\text{s}$ ), and reading the temperature correspondent to  $\xi_g = 0.5$ . Up to  $10^{\circ}\text{C}/\text{min} = 0.167^{\circ}\text{C}/\text{s}$  the data fully superposed to the model prediction. Larger cooling rates causes the model to predict semi-crystallization temperatures lower than the experimental ones.

The use of low mass samples has minimized the heat transfer resistance *inside* the sample, but the heat transfer resistance *outside* the sample has to be taken into account. The correction suggested by Eder *et al.* [5], i.e. the equation (6), to calculate  $\xi_g$ , and the equation (8), to calculate  $T_s$ , have been applied to the raw data (the continuous line in Figure 2), and the semi-crystallization temperatures obtained are reported in Figure 3 as open triangles. Up to  $10^{\circ}\text{C}/\text{min} = 0.167^{\circ}\text{C}/\text{s}$  these 'corrected' data superposed to both the 'uncorrected' data and to the isothermal model

predictions. At larger cooling rates, on the basis of the 'corrected' data, the crystallinity develops at temperatures higher than the ones which results from the 'uncorrected' data. This circumstance deserves an important remark: working at the highest cooling rates allowed to a DSC, even if the sample is very small, the data observed can be consistently far from real material behaviour. It means that, although the modern DSC can control the cooling rate up to 120°C/min (2°C/s), the crystallization kinetics observed could be fully meaningless!

At this point of the analysis, the most reliable data should be the 'corrected' ones. However, these temperatures are considerably larger than the ones predicted by the model. On the basis of different experiments carried out at larger and not constant cooling rates, it has been demonstrated [12] that the isothermally tuned model has to be modified to take into account non-isothermal effect, which is well described by an enhancement of nuclei density due to the cooling. This enhancement has been modelled [12] by equation (9) (values of parameters  $\alpha$  and  $\beta$  are reported in Table 1):

$$N(T, \dot{T}) = N(T) \left[ 1 + \alpha (-\dot{T})^\beta \right] \quad (9)$$

The predictions of the non-isothermal model, given by equations (1-4) plus (9), are reported in Figure 3 as dashed line. They compares nicely with the 'corrected' data. It is worth noticing that the model was tuned independently from the results of this work, but it is in full agreement with the data obtained here.

## 5. Conclusions

Some constant cooling rate solidification tests have been carried out in a DSC apparatus, using a very little amount of iPP shaped as thin disks. Thus, the heat transfer resistance into the samples have been minimized; whereas a model correction taken from literature [5] have been adopted to account for the external heat transfer resistances, i.e. between the sample, the pan and the DSC furnace. The differences observed between 'old', 'new uncorrected' and 'new corrected' experimental data bring to the following recommendation. Care must be taken to assure that the observed data describe the real material behaviour: i) the tests have to be performed working with very little amount of material; ii) the heat transfer phenomena between the sample and the furnace have to be taken into account.

The corrected data demonstrated that the crystallization takes place at temperatures higher than the ones suggested by a previous, less careful analysis (carried out using larger samples and a less accurate DSC apparatus), in agreement with the recommendation theoretically predicted in a previous work [1].

The 'new corrected' data have been used to check the validity of a crystallization kinetic model, tuned under isothermal conditions [2], confirming that, for cooling rates less than 10°C/min (0.167 K/s) the model can describe also non-isothermal tests; but faster cooling requires a modification of the model equations.

## References

1. Lamberti G. Heat and Mass Transfer 2004; 41: 23-31.
2. Lamberti G. Polymer Bulletin. 2004; 52(6): 443-449.
3. Alfonso GC, Ziabicki A 1995, Colloid Polym Sci 273:317-327.
4. Lamberti G, Brucato V, 2003, Journal Polym Sci B Polym Phys, 41(9):998-1008.

5. Eder G, Janeschitz-Kriegl H. In: Meijer HEM, editor. *Materials science and technology*, vol. 18. New York: Wiley, 1997. Chap. 5, pp. 269-342.
6. Kolmogoroff AN. *Izvestiya Akademii Nauk SSSR Ser. Math.* 1937; 3:355-360.
7. Avrami M. *Journal Chem. Phys.* 1939; 7: 1103-1112, *ibidem* 1940; 8: 212-224, *ibidem* 1941; 9: 177-184.
8. Evans UR *Trans Faraday Soc.* 1945; 41:365-374.
9. Hoffmann JD, Davis GT, Lauritzen JI. In: Hannay NB, editor. *Treatise on Solid State Chemistry*, vol. 3. New York: Plenum Press, 1976. Chap.7, pp. 497-614.
10. Chan T.W., Isayev A.I. *Polymer Engineering Science* 1994; 34: 461-471.
11. Lamberti G. "Flow induced crystallization and transformation of thermoplastic polymers", Ph.D. thesis (in Italian), CUES, Salerno, 2000.
12. Lamberti G. "New trends in modeling the polymer crystallization kinetics and its impact on polymer processing", to appear in *Recent Research Developments in Applied Polymer Science*, Volume 3, 2005.