

## ISOTHERMAL CRYSTALLIZATION KINETICS OF LOW VISCOSITY POLYAMIDE 66

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### Abstract

*The crystallization of polymers is commonly restricted in between the equilibrium melting temperature of crystals and the glass transition temperature. Study of the isothermal crystallization, close to the glass transition temperature, is complicated since nucleation and crystallization must be avoided during the approach of the temperature of interest. It requires cooling at a rate, which is distinctly higher than the maximum rate of nucleation. In fact, the cooling capacity of standard differential scanning calorimetry (DSC) is often insufficient to highly super cool the melt before onset of nucleation or ordering processes. For that reason, the Flash DSC 1 was used, where the cooling rate can reach more than 1000 Kelvin per second, which has allowed studying the isothermal crystallization kinetics in a large temperature range.*

### 1. Introduction

Nowadays, the levels of performances achievable with continuous reinforcement composite are well demonstrated. Among these composites, it is recognized that the use of thermoplastic matrix is a major advantage because of their low environmental impact (no VOC and solvent) and good resistance to crash (intrinsic ductility). However, the use of these materials is strongly limited for applications involving mediums for large production series (e.g. automotive industry). More precisely, the high viscosity of melted polymers, currently available, makes it extremely difficult to impregnate the reinforcements (performs), especially

when fiber content is high ( $> 50$  vol.%), which is most required for structure parts applications. Among the interesting manufacturing methods of composite structures, Liquid Composite Molding (LCM)[1][2][3] is of major interest to produce parts with complex geometry. The very recent development of new polyamide-based thermoplastic polymers with low viscosity ( $\eta=10$  Pa.s) enables the access to these ways of processing. Part quality and production rate are strongly linked to the thermal history during the molding. Therefore, accurate description of heat transfer is a key point to succeed in simulation and optimization of process. Therefore, process simulation requires full and accurate knowledge of thermo-physical properties and phase change due to crystallization to provide coherent results.

Within this framework, the measurements of exotherms are made with classical Differential Scanning Calorimeter (DSC) under isothermal conditions to classically determine the Avrami kinetic function and the Avrami coefficient at high temperature crystallization. However, this method cannot survey the whole temperature range (especially low crystallization temperature) encountered in composite forming processes. Therefore, a commercial nano-calorimeter, Flash DSC 1[4][5], has been used for the first time to follow the isothermal crystallization of PA66 from  $100^{\circ}\text{C}$  to  $220^{\circ}\text{C}$ . New crystallization kinetics results are compared with classical DSC, to check if they are in good agreement.

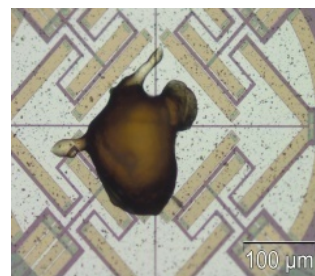
## 2. Experimental section

### 2.1. Fast scanning calorimetry

For FSC analyses, we employed a Mettler-Toledo Flash DSC 1 instrument, with the particular device including the sensor described in detail in the literature[4][5]. Briefly, the Mettler-Toledo Flash DSC 1 is a twin-type chip calorimeter, operating in power-compensation mode. The sample was prepared from granule of PA 66 under integrated microscope and placed in the center of the sensor chip Fig 1.a. The sample is melted at a low heating rate ( $10$  K/s). A larger sample is necessary to study the isothermal crystallization, considering the heat flow is very small. Therefore, the material was added with the same procedure to increase the mass of the sample Fig 1.b.



**Fig.1.a.** Sample preparation method



**Fig.1.b.** Microscopy photograph of PA 66 sample prepared for the Flash DSC 1

## 2.2. Flash DSC 1 calibration

The Flash DSC 1 sensor is calibrated with a piece of indium placed on the reference part of the chip sensor. The sensor chip is then heated at various scanning rates and the onset-melting peak is measured, the evolution of  $\Delta T$  versus the heating rate gives the following relation

$\Delta T = 6.43 \times 10^{-3} \times \frac{dT}{dt} - 0.554$ , where  $\Delta T$  is the difference between the theoretical and the experimental melting temperature  $\Delta T = T_{m,theo} - T_{m,XP}$ .

## 2.3. Mass estimation

The mass of the sample was estimated from the heat capacity equation 1. Where the heat capacity of PA 66 was identified before by measurements made on classical DSC. Therefore, the mass was estimated at 690 [ng].

$$m = \frac{\Phi_e - \Phi_r}{C_p \frac{dT}{dt}} \quad (1)$$

Where, the  $\Phi_e$  is the heat flux supplied to the sample [ $mW$ ],  $\Phi_r$  is the heat flux supplied to the reference [ $mW$ ],  $m$  is the mass of the sample [ $mg$ ] and  $C_p$  is specific heat capacity [ $J.g^{-1}.K^{-1}$ ].

## 3. Experimental procedure measurements

The isothermal crystallization of PA 66 was studied with the temperature cycle shown in Fig.2.a and Fig.2.b. First, the polymer remains 0.1 s at 300 °C to erase the thermal history of the sample, particularly to melt all crystals. The applied scanning rate is 2000 K/s for both heating and cooling. The isothermal crystallization was studied by two methods depending on the crystallization temperature chosen. The first method is the direct method where we apply the classical cycle as shown in the Fig.2.a. This method was used when the flow of crystallization is large enough and applied when the temperature of crystallization is between 120 and 210 °C. Another method, which was used when crystallization heat flow is too small, is called in this paper the ‘discrete method’. The experimental protocol of this method is explained in the Fig2.b. After having chosen the crystallization temperature this cycle is repeated with changing the crystallization time. The crystallized ratio was calculated in this case from the melting enthalpy. This method was applied for temperatures 100-110 and 220 °C. The heating and cooling rate was 1000 K/s.

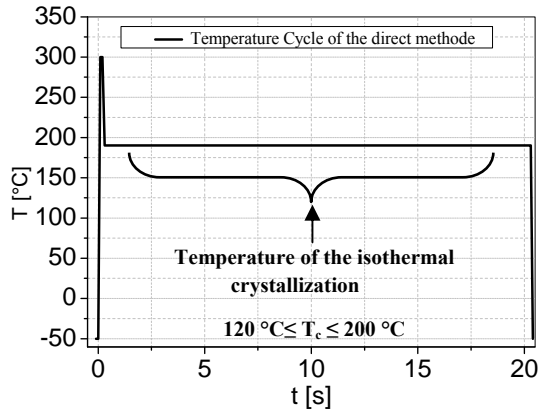


Fig. 2a. Temperature cycle used for the direct method

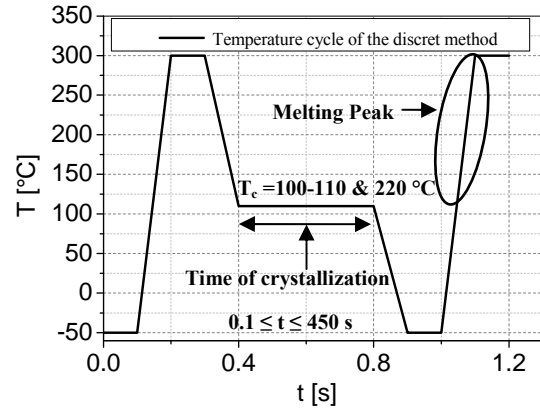


Fig.2b. Temperature cycle used for the discrete method

#### 4. Results and analysis

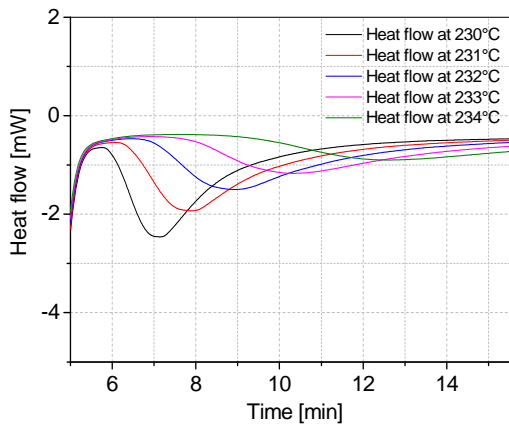
Firstly, the procedure is applied for isothermal crystallization between 120 °C and 210 °C. The heat flow is directly measured from the isothermal crystallization peak. The relative crystallinity is calculated from the equation 3, where  $t_1$  and  $t_2$  are the limits of the heat flow integration.  $\Delta H_T$  is the enthalpy of crystallization measured by the whole integral of crystallization peak.

$$\alpha(t) = \frac{\int_{t_1}^{t_2} dh}{\Delta H_T} \quad (3)$$

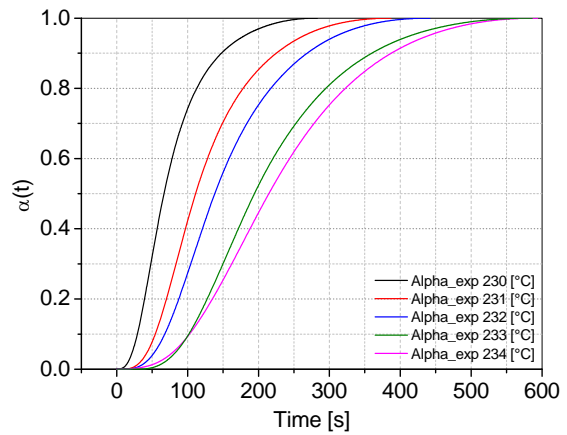
The kinetics of isothermal crystallization is described by Avrami [6][7][8], equation 4.

$$\alpha(t) = 1 - \exp(-K_{Av} \cdot t^n) \quad (4)$$

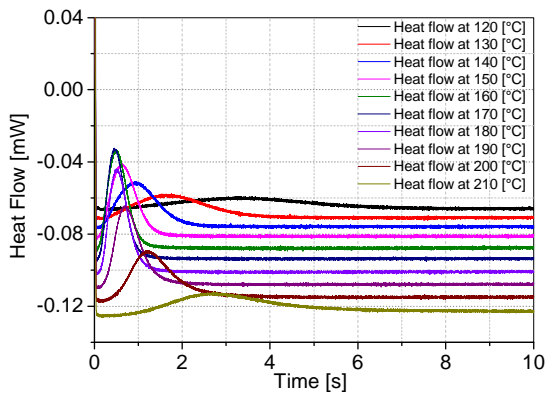
In this equation,  $K_{Av}$  is the Avrami coefficient that depends on the temperature and  $n$  is the Avrami exponent, which describes the growth mode of the crystalline entities and the nature of the nucleation. Generally, the PA 66 had an instantaneous germination and the spherulites have a spherical shape. Therefore,  $n$  the exponent of Avrami should be close to 3. Wherever, The Avrami exponent  $n$  and  $K_{Av}$  coefficient are estimated by plotting  $\ln(-\ln(1-\alpha)) = \ln K_{Av} + n \ln t$ . The slope of the curve gives the  $n$  value and the offset gives the  $K_{Av}$  value. The Fig 3.a and Fig. 3.b show the experimental heat flow and the of  $\alpha(t)$  evolution for the several crystallization temperature obtained on DSC TA Q200. The Fig. 4.a, Fig. 4.b, Fig 4.c and Fig 4.d show the experimental results obtained on Flash DSC 1 by the direct and discrete method.



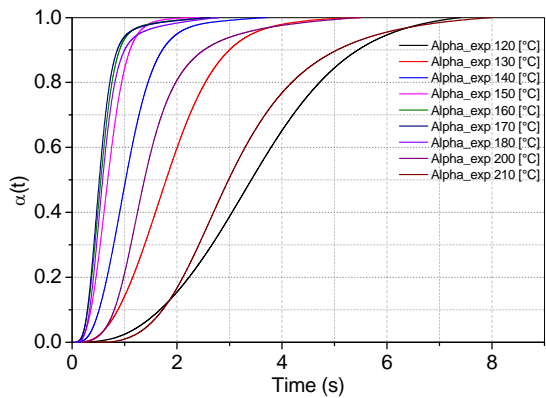
**Fig. 3.a.** Heat flow of the isothermal crystallization of PA 66 between 230 and 234 °C, measurements made on Classical DSC TA Q200



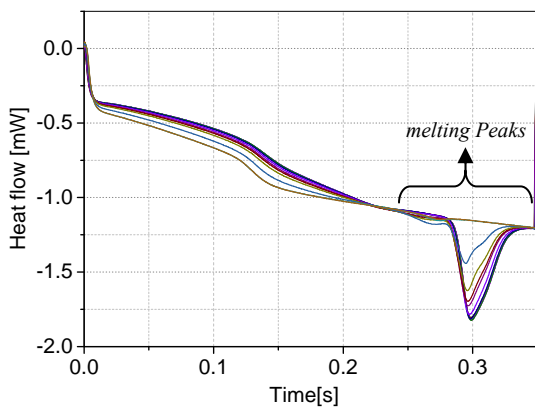
**Fig. 3.b.** Relative crystallinity of PA 66 after isothermal crystallization



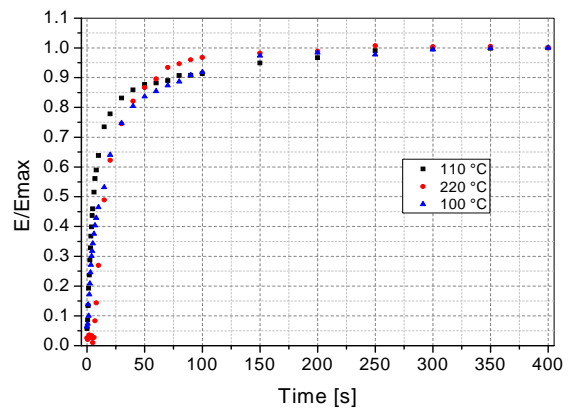
**Fig. 4.a.** Heat flow of isothermal crystallization of PA 66 between 120 and 210 °C made on Flash DSC 1 by Direct method



**Fig. 4.b.** Relative crystallinity of PA 66 after isothermal crystallization made on Flash DSC 1 by the direct method



**Fig. 4.c.** Heat flow of isothermal crystallization of PA 66 at 100, 110 and 230 °C made on Flash DSC 1 by the discrete method



**Fig. 4.d.** Heat flow for each crystallization time measured by the discrete method at 100, 110 and 220 °C

From the results of the discrete method the heat flow for each melting peak was determined. The evolution of the melting flow versus time of crystallization was drawn on the Fig 4. From these curves, whereas the half-time crystallization can be directly determined. In the other hand, from the results obtained by using the direct method, n and the half time crystallization were determined, and then  $K_{Av}$  is calculated by the equation 5:

$$K_{Av} = \sqrt[n]{\frac{\ln 2}{t_{1/2}}} \quad (5)$$

The half time crystallization, the Avrami exponent 'n' and  $K_{Av}$  are summarized in the table 1, 2 and 3.

Temperature [°C]	n	$K_{Av}[s^{-n}]$	$t_{1/2}[s]$	$\Delta H_C [mJ]$
120	2.62	4.29E-02	2.9	0.0212
130	2.43	2.26E-01	1.6	0.0221
140	2.53	8.68E-01	0.9	0.0276
150	2.65	2.45E+00	0.6	0.0279
160	2.73	5.15 E+00	0.5	0.0305
170	2.93	7.33 E+00	0.4	0.0304
180	3.07	5.75 E+00	0.5	0.0318
190	2.81	1.85 E+00	0.7	0.0319
200	2.91	4.22E-01	1.2	0.0311
210	3.08	3.24E-02	2.7	0.0336

**Table 1:** Half time crystallization, n and  $K_{Av}$  values for the measurements with Flash DSC by the direct method

Temperature [°C]	n	$K_{Av}[s^{-n}]$	$t_{1/2}[s]$	$\Delta H_C [J/g]$
230	2.49	2.26E-05	63.4	32.5
231	2.96	7.22E-07	105.6	26.7
232	2.94	4.03E-07	131.8	23.9
233	3.38	1.57E-08	183.8	22.7
234	2.75	1.97E-09	240.4	19.3

**Table 2:** Half time crystallization, n and  $K_{Av}$  values for the measurements with classical DSC TA Q200

Temperature [°C]	$t_{1/2}[s]$	$K_{Av}[s^{-n}]$
100	12.5	1.27E-03
110	6.3	6.96E-03
220	11.4	1.58E-03

**Table 3:** Half time crystallization and  $K_{Av}$  values with Flash DSC 1 by the discrete method

According to all these measurements obtained with Flash DSC 1 and with the classical DSC, it has been shown that the half time crystallization is in good agreement for the two apparatus, see Fig.5.a and Fig. 5.b.

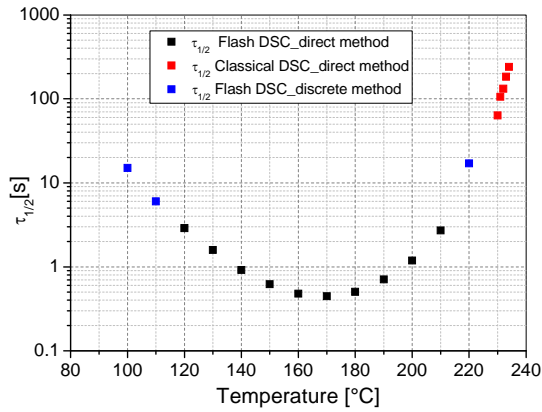


Fig. 5.a. Half-time crystallization versus the crystallization temperature

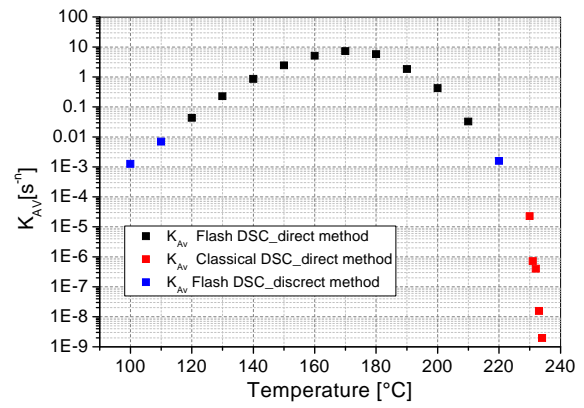


Fig. 5.b. Avrami coefficient and Avrami exponent of versus the temperature

It was interesting to study the influence of the mass of the sample on the results of Flash DSC 1. Therefore, a comparison is made between two samples such that each sample has a different mass of the other Fig.6.

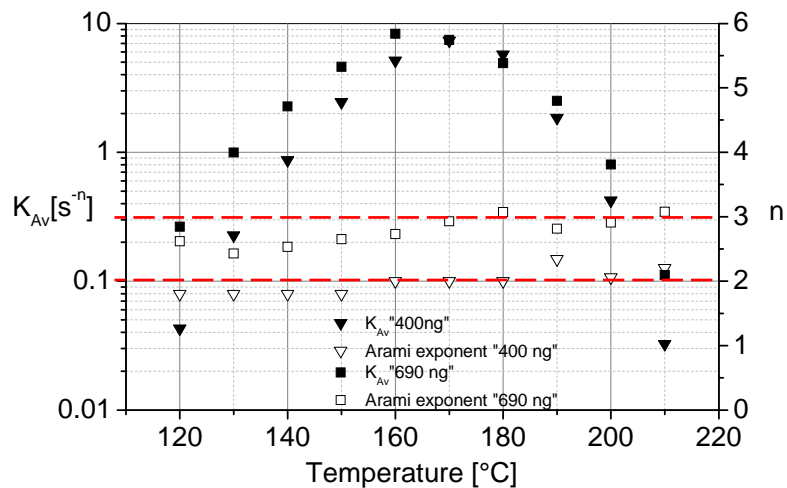


Fig.6. Comparison of the Avrami coefficient " $K_{Av}$ " and the Avrami exponent " $n$ " for two samples having different masses

Based on this result, it was noticed that when the mass of polymer is small, the Avrami exponent,  $n$ , was close to 2. This could be interpreted as the growth of the spherulites in two dimensions, or due to transcrystallinity presence between the polymer and chip sensor [9]. On

the other hand, when the polymer mass is large enough the Avrami exponent was close to 3 which means that the spherulites have a 3D growth.

## 5. CONCLUSION

In this study, the isothermal crystallization kinetics of low viscosity PA 66 has been studied by using the Flash DSC 1. It has been studied on a large temperature domain. Two methods have been employed in this study. One of them used when the crystallization heat flow is large enough called "direct method". The other one was used called "discrete method". The half-time crystallization and the Avrami kinetics function have been evaluated from isothermal crystallization between 100 and 220 °C whereas previous data were not available in this range. The Avrami exponent,  $n$ , was around 3 that suggest a spherical growth with an instantaneous nucleation. The results of the half-time crystallization, the Avrami function and of the Avrami exponent obtained by using the Flash DSC 1 were compared with the results obtained by classical DSC. According to these results, it was noticed that the measurements of Flash DSC 1 and the classical DSC are well in agreement. The mass of the Flash DSC 1 sample was estimated. It was noticed that the mass of the Flash DSC 1 sample has a very important influence on the obtained results; specifically it affected the growth of spherulites.

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