



## Parametric study of the crystallization kinetics of a semi-crystalline polymer during cooling

### *Étude paramétrique de la cinétique de cristallisation de polymères semi-cristallins lors du refroidissement*

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#### ABSTRACT

During the cooling stage in several types polymer processing, the behavior of the polymer is very difficult to model and to simulate numerically, because of the complicated coupling between the crystallization process, the heat transfer and the material properties change. The aim of this Note is the numerical simulation of the coupling phenomena between the crystallization rate and the thermal kinetics in a semi-crystalline polymer during cooling without flow, by using Finite Elements Method.

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#### R É S U M É

Au cours de l'étape de refroidissement lors de la transformation des polymères, le comportement du matériau est difficile à modéliser, à cause du couplage complexe entre les phénomènes de cristallisation, les transferts thermiques et les variations des propriétés du matériau. Ce travail porte sur la simulation numérique du couplage entre la cinétique de cristallisation et la cinétique des transferts thermiques, en l'absence d'écoulement et en utilisant la méthode des éléments finis.

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## 1. Introduction

The computer simulation of polymer processing is an essential tool to predict the properties of the final product. For an adequate calculation, one needs to make a coupling between several physical phenomena: phase change, crystallization, thermodependency of several parameters like the viscosity, the density, the heat capacity and the thermal conductivity. The knowledge of the rheological and thermophysical material characteristics is then of great importance. To understand the crystallization process of semi-crystalline thermoplastics, it is necessary to take into account the kinetics of crystallization and to consider the temperature and crystallization dependency of all the thermophysical properties of the material. All these variable parameters make the simulation more complicated. Generally, the simulations are simplified by considering isothermal or isobaric cases. In this work we have employed multiphysics software based on FEM method to study the coupling between heat transfer and crystallization kinetics during the solidification of a semi-crystalline polymer, such as

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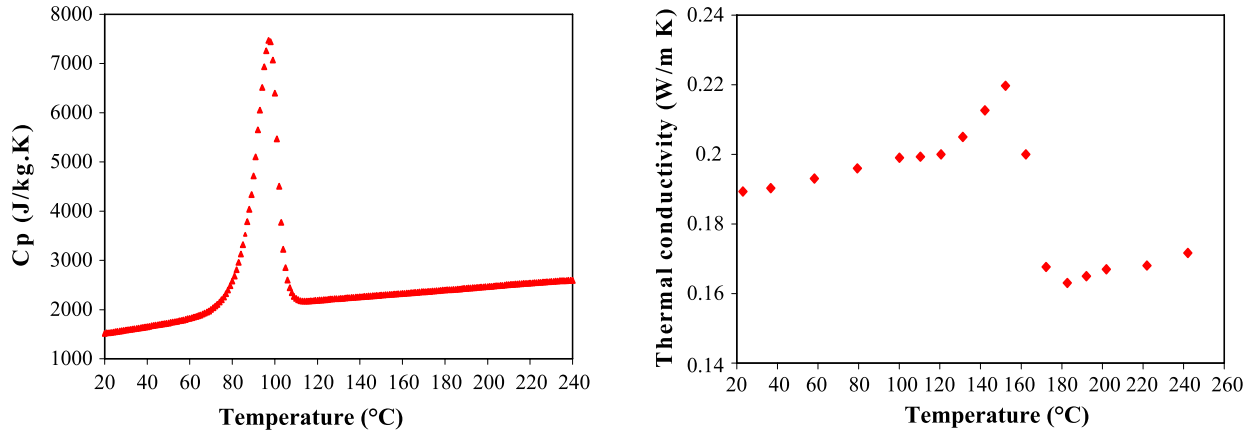


Fig. 1. Evolution of the heat capacity (a) and the thermal conductivity (b) versus temperature.

Fig. 1. Evolution de la chaleur massique (a) et de la conductivité thermique (b) avec la température.

polypropylene. First, the polymer studied was precisely characterized and the parameters of the model of crystallization are identified, using Differential Scanning Calorimetry (DSC) experiments. The results are compared to some data find in the literature, Fulchiron et al. [1] in controlled thermal conditions, and then the model is generalized to any non-isothermal conditions in order to study the influence of several parameters on the polymer crystallization.

## 2. Polymer characterization

To study heat transfer during crystallization of a polymer, it is necessary to take into account its thermal properties as a function of temperature and relative crystallinity  $\alpha$ . At atmospheric pressure, the heat capacity is described using simple mixing rule between the solid state and the liquid state values weighted by the relative crystallinity  $\alpha$ :

$$C_p(\alpha, T) = \alpha C_{psc}(T) + (1 - \alpha)C_{pa}(T) \quad (1)$$

where  $C_{psc}$  and  $C_{pa}$  are the heat capacity of the solid state and the liquid state, respectively.

The specific heat  $C_p$  in each phase of the polymer was obtained using DSC measurements as shown in Fig. 1a.

For the polymer used in this work, Le Bot [2] proposed a linear temperature dependency versus temperature for  $C_{psc}$  and  $C_{pa}$ , their values are:

$$\begin{cases} C_{pa}(T) = 3.4656T + 1774.2 \\ C_{psc}(T) = 8.3619T + 1329.2 \end{cases} \quad (2)$$

with  $T$  in degree °C and  $C_p$  in  $\text{J kg}^{-1} \text{K}^{-1}$ .

The thermal conductivity ( $\lambda$ ) was measured by an apparatus based on the transient "line source method", which is ideally suited to polymers because measurements can be made quickly, before the onset of thermal degradation and no sample preparation is required [3].

$\lambda$  is also described by a mixing rule between solid state and liquid state as follows, but other methods [4] leading to closely similar results can be used:

$$\begin{cases} \lambda(T, \alpha) = \alpha \lambda_{sc}(T) + \lambda_a(T) \\ \lambda_{sc}(T) = 10^{-4}T + 0.1868 \\ \lambda_a(T) = 10^{-4}T + 0.1394 \end{cases} \quad (3)$$

where  $\lambda_{sc}$ ,  $\lambda_a$  represent, respectively, the thermal conductivity of amorphous and semi-crystalline phase, and are temperature dependent as in Fig. 1b.  $T$  in °C and  $\lambda$  in  $\text{W m}^{-1} \text{K}^{-1}$ .

The specific volume (density inverse) which is deduced from PVT diagram was evaluated as a weighted mean value of the pure amorphous and crystalline values according to:

$$\begin{cases} V(\alpha, T) = \alpha V_{sc}(T) + (1 - \alpha)V_a(T) \\ V_a(T) = 3 \times 10^{-3}T + 1.2108 \\ V_{sc}(T) = 2.6 \times 10^{-3}T + 1.1055 \end{cases} \quad (4)$$

where  $T$  in °C and  $V$  in  $\text{m}^3 \text{kg}^{-1}$ ,  $V_a$  and  $V_{sc}$  are, respectively, the specific volume of the amorphous sate and the solid state estimated from the PVT measurements.

The PVT experimental results were obtained using a piston-type dilatometer (GNOMIX®).

### 3. Crystallization kinetics

The overall crystallization kinetics theories describe the evolution of the relative crystallinity  $\alpha(t)$  as a function of time and temperature. This relative crystallinity is defined as the ratio of the crystallized volume  $X_c$  to the ultimate crystallizable volume  $X_\infty$ :

$$\alpha = \frac{X_c(t, T)}{X_\infty} \quad (5)$$

Two types of approaches were employed during the development of the global theories of crystallization kinetics: the geometrical approach, which express the volume occupied by the semi-crystalline entities, and the probabilistic approach, which calculates the probability that an element of volume is transformed. The main differences lie in the mathematical treatment, but the basic assumptions and especially the results are identical.

The geometrical approach considers the free growth of crystalline entities of simple geometries, and then applies a correction taking into account the so called impingement (i.e. the fact that the growth of each entity is not free, but blocked by the contact with the close entities).

For a finite volume, the variation of the crystallinity  $d\alpha$  is related to the variation of the crystallinity for an infinite available volume  $d\alpha'$  by:

$$d\alpha = (1 - \alpha) d\alpha' \quad (6)$$

This expression can be integrated versus time and gives:

$$\alpha(t) = 1 - \exp(-\alpha'(t)) \quad (7)$$

$\alpha'$  is a fictitious crystallinity, obtained for a crystallite free growth. Eq. (3) represents the basis of all the Avrami type models [5].

In the probabilistic approach, Kolmogorov [6] and Evans [7] chose to calculate the probability that a representative point of a volume is crystallized. They assume that with a good approximation, this probability represents the crystallinity  $\alpha(t)$ .

Billon in [8] showed that the two theories of Evans and of Avrami, are equivalent because they are implicitly based on the same assumptions. In this work, the global approach of Avrami is used. One limit of this theory is the fact that it doesn't takes into account the flow effect on the polymer crystallization, but only the temperature effect, and considers that the rate of the crystallite growth is constant, and not effected by the temperature.

To describe polymer crystallization kinetics under non-isothermal, isokinetic conditions, Nakamura et al. [9] developed the following equation from Avrami theory [5]:

$$\alpha(t) = 1 - \exp\left(-\left(\int_0^t K(T) d\tau\right)^n\right) = 1 - \exp\left[-\left(\int_0^t \ln(2)^{\frac{1}{n}} \left(\frac{1}{t_{1/2}}\right) dt\right)^n\right] \quad (8)$$

where  $n$  is the Avrami index,  $t_{1/2}$  is the crystallization half time, and  $K(T)$  is the non-isothermal crystallization rate constant.

By assuming that the number of nucleation sites is independent of temperature and all sites are activated at the same time, Hoffman et al. [10] developed the following expression to describe the overall rate of crystallization as a function of temperature:

$$\left(\frac{1}{t_{1/2}}\right) = \left(\frac{1}{t_{1/2}}\right)_0 \exp\left(\frac{-U^*}{R(T - T_\infty)}\right) \exp\left(\frac{-K_g}{T\Delta T}\right) \quad (9)$$

where  $T$  is the crystallization temperature,  $R$  is the universal gas constant,  $U^*$  is the activation energy of the transport of crystallizing units across the phase boundary.  $T_\infty$  is the temperature under which such as transport ceases.  $K_g$  is the spherulite growth rate,  $\Delta T = T_f^0 - T$  is the super cooling. According to Hoffman et al. [10] the parameter  $U^*$  and  $T_\infty$  can be assigned "universal" values 6284 J/molK and  $T_g - 30$  K respectively.  $T_g$  is the glass transition temperature of the material.

Differentiation of Eq. (8) leads to differential form of Nakamura crystallization kinetics, which is more useful in modeling:

$$\frac{\partial \alpha}{\partial t} = nK(T)(1 - \alpha)^{\frac{n-1}{n}} [-\ln(1 - \alpha)]^{\frac{n-1}{n}} \quad (10)$$

with

$$K(T) = \ln(2)^{\frac{1}{n}} \left(\frac{1}{t_{1/2}}\right) \quad (11)$$

To determine  $K(T)$ , different DSC measurements of isothermal and non-isothermal crystallization were carried out, following a measurement protocol used previously by Koscher [11,12]. By fitting the experimental results using Eqs. (9) and (11) and an optimization algorithm based on the Levenberg–Marquardt method [13,14], the parameters which permitted to determine  $K(T)$  were identified.

In order to identify generalized parameters, the DSC measurements are carried out in isothermal and non-isothermal conditions, and under several cooling rates.

#### 4. Mathematical modeling

The general energy equation has been used to describe the heat transfer in the system:

$$\rho(\alpha, T)C_p(\alpha, T) \frac{\partial T}{\partial t} = \frac{\partial}{\partial y} \left( \lambda(\alpha, T) \frac{\partial T}{\partial y} \right) + \rho(\alpha, T) \Delta H \frac{\partial \alpha}{\partial t} \quad (12)$$

$\Delta H$  is the total enthalpy released during crystallization process.

The crystallization kinetics is given by Nakamura equation as follows:

$$\frac{\partial \alpha}{\partial t} = nK(T)(1 - \alpha)(-\ln(1 - \alpha))^{\frac{n-1}{n}} \quad (13)$$

The Nakamura constant  $K(T)$  can be expressed by:

$$K(T) = \left( \frac{4}{3} \pi N_0(T) \right)^{\frac{1}{3}} G_0 \exp\left( -\frac{U^*}{R(T - T_\infty)} \right) \exp\left( -\frac{K_g}{T(T_f^0 - T)} \right) \quad (14)$$

The polymer tested by Koscher [11,12] is an injection grade of isotactic polypropylene (Eltex HV 252). The values of different parameters in  $K(T)$ , are listed as follows:  $N_0(T) = \exp(0.156 \times (T_f^0 - T) + 15.1)$ ,  $G_0 = 2.83 \times 10^2$ ,  $K_g = 5.5 \times 10^5$  (K<sup>2</sup>),  $U^* = 6284$  J/molK,  $T_f^0 = 210$  °C,  $T_\infty = -30$  °C,  $\Delta H = 90 \times 10^3$  J/kg and  $n = 3$ . The material properties are then completely identified.

#### 5. Results and discussion

##### 5.1. Comparison with experimental results

To ensure that the FEM method solves correctly the problem, without any numerical errors, a first validation is made by comparison of calculations with those obtained using finite differences method with self made software.

The second validation of the model is made by comparison with experimental results from literature [12]. Due to the lack of data obtained in similar systems, the configuration was simplified. We have assumed that the system is cooled at constant cooling rate as in a differential scanning calorimeter (DSC). The temperature is homogeneously distributed in the polymer, and decreases linearly:  $T = T_0 - V_{cool} \times t$ , where  $T_0$  represent the initial temperature of the system and  $V_{cool}$  is the cooling rate value.

The relative crystallinity was calculated for several constant values of cooling rates and temperatures. Comparison between our simulations results, Koscher et al. [11] experimental results and their own calculations were carried out as shown in Figs. 2a and 2b.

For constant cooling rate, our calculations were more representative of the experimental results, compared to those calculated in the literature. This simulation permitted to improve the calculation of crystallization kinetics, by insuring a real coupling between the crystallization and the heat transfer taking into account the material parameters evolutions versus temperature. In Fig. 2, we can see that the FEM calculations curves follow with a good agreement the experimental data. This results, allows us to be confident in the application of the model in any non-isothermal conditions.

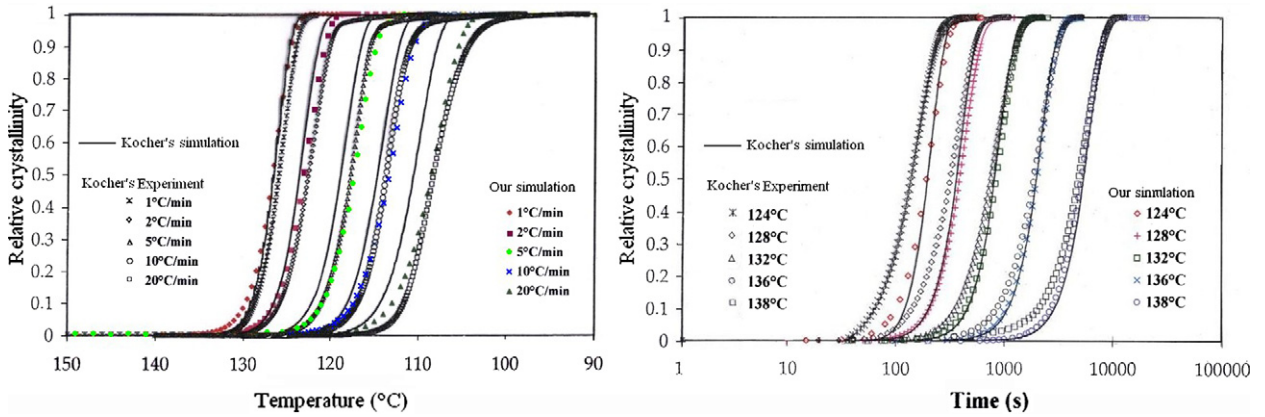
##### 5.2. Simulation of effective cooling of the polymer plate: coupling of the heat and the crystallization equations

The system is composed of a plate of polymer between two metal blocks. The thickness of each block is of 30 mm, and of the plate is of 5 mm.

- At initial time, the temperature of all the system is homogeneous  $T(t = 0) = T_0$ .
- The cooling boundary conditions are imposed at the interface metal/polymer. Due to the plate dimensions, the heat transfer occurs only by conduction in the thickness direction.
- Because it does not affect the aim of this study, a negligible contact thermal resistance is assumed between the polymer and the metal.
- In order to control the thermal kinetics in the polymer, we have assumed a linear decrease of the temperature at the interface metal/polymer as follows:  $T = T_0 - V_{cooling} \times t$  ( $V_{cooling}$  is the cooling rate).

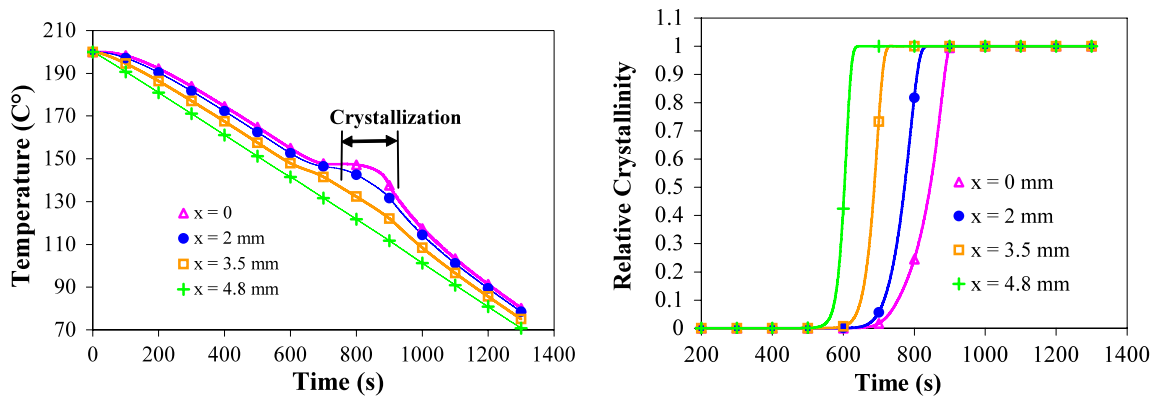
Fig. 3a shows the temperature evolution in the plate during the cooling process, at several locations in the thickness. At the middle of the plate (at  $x = 0$ ), due to the polymer thermal inertia, the temperature diminution begins after 60 s. The crystallization phase is characterized by a plateau that appear at 147 °C, and which corresponds to the release of latent heat of crystallization. After 920 s the polymer is entirely solidified and tends to be thermally homogeneous.

Fig. 3b presents the evolution of relative crystallinity as function of time at different locations in the plate. We notice that the polymer in the skin layer crystallizes more quickly then in the core layer. The total crystallization time is about 180 s.



**Fig. 2.** Comparison for several constant cooling rates (left) and isothermal crystallization (right) of relative crystallinity: our results, Koscher measurements and Koscher calculations [11].

**Fig. 2.** Comparaison à différentes cinétiques de refroidissement (gauche) et à cristallisation isotherme (droite) de la cristallinité relative : nos résultats, les mesures et calculs de Koscher [11].



**Fig. 3.** Temperature (left) and relative crystallinity (right) at different locations in the polymer, ( $V_{\text{cooling}} = 6^\circ\text{C}/\text{min}$ ).

**Fig. 3.** Température (gauche) et cristallinité relative (droite) à différentes positions dans le polymère ( $V_{\text{cooling}} = 6^\circ\text{C}/\text{min}$ ).

### 5.3. Effect of the cooling rate

The effect of the thermal kinetics on the crystallization rate can be observed in Figs. 4a and 4b. As expected, we observe that the decrease in initial temperature leads to the acceleration of the crystallization and conversely. The cooling time is reduced of about (242 s) when we increase the  $V_{\text{cooling}}$  of about  $18^\circ\text{C}/\text{min}$ .

For the relative crystallinity at the polymer core for different cooling rates, Fig. 4b shows that the crystallization is shifted to the lower temperatures when the cooling rate is more important. A difference of  $10^\circ\text{C}$  between the corresponding temperatures of the half-time transformation is observed, for two different thermal kinetics:  $V_{\text{cooling}} = 12^\circ\text{C}/\text{min}$  and  $V_{\text{cooling}} = 30^\circ\text{C}/\text{min}$ .

### 5.4. Effect of initial temperature

To explore the polymer thermal history, we have studied the effect of the initial temperature in the material behavior, Fig. 5. It's clear from the evolution of the temperature profile in the polymer core, that initial temperature affects drastically the cooling kinetics. When  $T_0$  increases, the crystallization begins with a delay, but the rate of cooling and the temperature of crystallization doesn't change.

Fig. 5b shows, the evolution of relative crystallinity at the interface (mould/polymer) and at polymer core. We note that crystallization begins approximately at the same temperature at the interface mould/polymer and also at the polymer core, but it continues on more important ranges of temperatures at the interfaces. Indeed, at the polymer core, crystallization plateau slow down considerably the cooling, so, the temperature changes less quickly, whereas crystallization continues. At the interface, temperatures decrease quickly, and the crystallization takes a large range of temperatures.

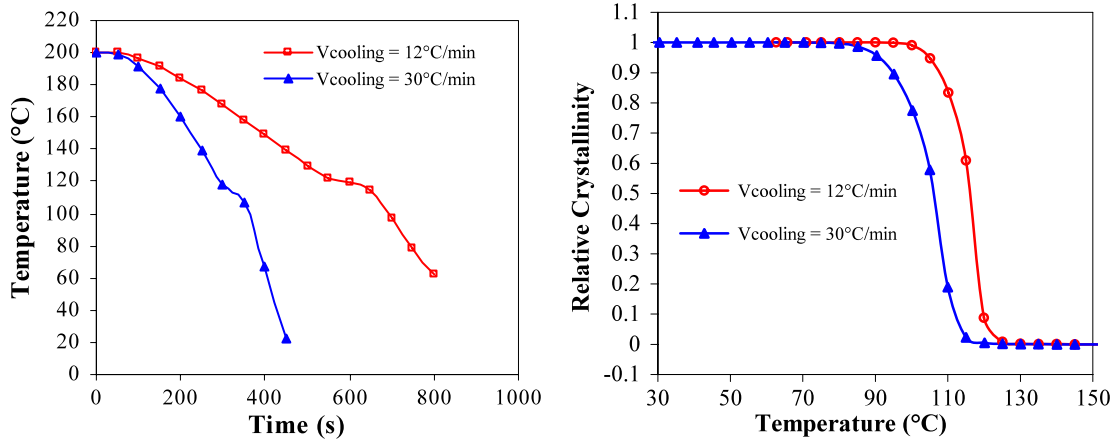


Fig. 4. Effect of the cooling rate on the temperature field (left) and crystallization (right) at polymer core layer.

Fig. 4. Effet de la vitesse de refroidissement (gauche) sur la température et la cristallisation (droite) dans la couche centrale.

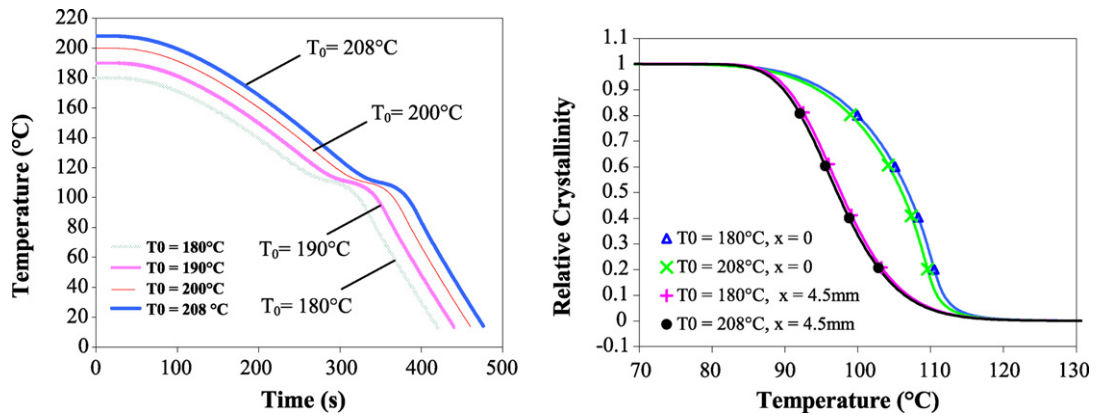


Fig. 5. Effect of initial temperature on temperature profile (left) and relative crystallinity (right) at polymer core layer.

Fig. 5. Effet de la température initiale sur la température (gauche) et la cristallinité relative (droite) au centre du polymère.

## 6. Conclusion

Multiphysics software based on finite elements method was used to simulate the cooling of a polymer as in the injection moulding process of a semi-crystalline polymer. To simplify the injection mould configuration, we have considered a one-dimensional heat transfer in a system of polypropylene plate, initially at melt temperature, cooled between two metallic blocks. To take into account crystallization process of the material, *Nakamura* differential equation was coupled to the equations system, where all the material parameters are temperature dependent. An important work of parameters measurement is made with their temperature dependency. Simulations permitted us to determine temperature profile and relative crystallinity evolution at different positions of the system. The good agreement between finite differences method calculations and FEM simulations, in a simplified case, permitted us to validate our numerical model in a DSC measurement configuration, and in controlled temperature condition. The model is then generalized to any non-isothermal conditions, which constitute an important step in the application of the crystallization models to real processes. The study of the effect of different parameters such as the initial temperature of the system and the cooling rate, on the crystallization was also carried out, and gives a clear and simple understanding of the polymer behavior during cooling. In spite of simplified *Nakamura* crystallization model (no flow effect), relative crystallinity had been well represented. This parametric study can be used to analyze in depth the structural gradient in plastic parts, and to connect their structure to their mechanical behavior. The difficulties of numerical simulations, with the direct coupling between the heat transfer equation and crystallization equation, are easily solved and interesting results and comparisons are obtained. The next objective will be to use a more developed crystallization kinetics model in a 3D simulation of the heat transfer in the injection molding process, by introducing the effect of the flow on the crystallization kinetics.

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