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Abstract

An estimation method of the thermal conductivity of polymers during their crystallization is presented in this paper. The outputs of the established method depict the evolutionary profile of the thermal conductivity function of two coupled fields: the temperature and the relative crystallinity. The identification relies on the thermal response registered within the polymer during its solidification. A unidirectional heat transfer model is developed for this purpose and the thermal response of the polymer is coupled with the exothermal heat generation taking place during the crystallization. A hybrid optimization algorithm combining a stochastic method with a deterministic one is adopted for the resolution of the inverse heat conduction problem. The potential of the estimation algorithm in solving a complex and non-linear problem is validated in this study. The robustness of the inverse method is evaluated by taking into account the measurement noise as well as the uncertainties on apriori known thermal parameters. A sensitivity analysis is presented to asses the accuracy of the inverse problem outputs and emphasize the relationship between the identifiable parameters and the imposed cooling rate.

Keywords: Thermal conductivity, Polymers, Crystallisation, Inverse method, Parameters estimation, Identification

1. Introduction

Identifying the thermophysical properties of polymer and composite materials has become an important matter and holds significant importance in several industrial applications. They contribute in many aspects such as the control and the validation of the manufacturing processes, the analyses of the thermal and/or mechanical stresses and shocks, the thermal fracture prevention, and the evaluation of manufactured material quality. The thermal behavior of thermoplastics is significantly influenced by their crystallinity. The solidified fraction affects the thermophysical properties in addition to temperature. Phonons are the average heat carriers in polymers, which are dielectric materials devoid of free electrons due to saturating systems. Therefore, their thermal conductivity is generally relatively low and ranges from 0.1 to 0.5 $W/(m.K)$ [1] [2] [3]. Since the configuration of the polymer crystalline region is more organized than the amorphous one and presents regular chain conformation, the mean free path of phonons within the crystalline region is increased [4] [5]. In this manner, the thermal conductivity of semi-crystalline polymers is greater than the amorphous one at the same temperature. Choy *et al*. [6] highlighted the dependence of the thermal conductivity on the temperature, the percentage of crystallinity and the chain alignment. The previous studies aimed to understand the variation of the thermal conductivity along the direction of the crystalline chains and in the direction perpendicular to the crystal function of temperature [7] [8] [9]. The thermal conductivity evolutions observed are related to several factors such as the difference between the covalent bonds and the Van der Walls bonds, the phonons Umklapp scattering [10] [11], the presence of crystal defects, the crystals dimensions, and other factors. Additionally, the effect of the chain alignment within a polymer has been widely investigated, particularly in the crystalline region

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[12] [13] [14]. However, the thermal conductivity values of semi-crystalline polymers figured in these studies are obtained at very low temperatures ($< 30\ K$). The thermal conductivity of polymer crystals has recently been investigated only at room temperature [15] [16].

The conventional characterization methods have been broadly used to investigate the variation of these properties in the amorphous state and in the semi-crystalline state as a function of temperature [4] [17] [18] [19]. These studies were conducted at temperatures ranging between the ambient and temperature levels greater than the melting points of the polymers. Prior experimental characterizations have been carried out to assess how temperature and crystallized fraction affect thermophysical property changes [20] [21]. The properties of the semi-crystalline polymers were estimated using discrete methods, not during crystallization, but rather in their final state with a fixed percentage of crystallinity.

Furthermore, the inclusion of the exothermal crystallization heat in the thermal problem is fundamental for coupling the temperature evolution with the crystallization. The resolution of the thermal problem necessitates the exact knowledge of the crystallization kinetics as well as thermophysical properties dependence on temperature and relative crystallinity. It is theoretically correct to model the volumetric heat capacity by the traditional mixing law [22]. However, this law can not be applied to the thermal conductivity since it is not an extensive property. Despite this, it is commonly used in thermal problems because of the slight difference in thermal conductivity between semi-crystalline and amorphous states[23]. Moreover, some authors modeled the effect of the crystallization on the thermal conductivity with the aid of models describing the conduction through heterogeneous media like composites. The fiber ratio is substituted by the relative crystallinity and the spherulites are assimilated to spherical crystallites embedded in an amorphous matrix. The classical models are Maxwell's model [24], Rayleigh's model [25], and Springer's model [26]. Le Goff *et al*. [23] compared the output of these models with the mixing rule and observed a negligible discrepancy among them.

The identification of thermophysical properties of polymer and composite materials is generally based on the resolution of an inverse heat conduction problem. A vast majority of the traditional inverse heat conduction problems aimed to identify the unknown thermophysical properties of materials in their final state. The solution of an inverse thermal problem relies on an experimentally measured sample's response to an excitation. In this manner, the laser flash coupled with a semi-analytical or a numerical model was broadly used to identify the unknown thermophysical properties of anisotropic materials [27] [28] [29]. Similarly, the transient plane source method was used by Tarasovs *et al*. [30] for this purpose. Others introduced numerical inversion models capable of identifying the components of the thermal conductivity tensor of a 3D anisotropic medium with an arbitrary shape [31].

Regarding temperature dependency, several methods were established to estimate the temperature-dependent thermophysical properties, by solving steady-state inverse heat conduction problems using a linear evolution[32] [33]. The evolution of the thermal conductivity of a thermoplastic, in its solid and liquid states, was investigated without taking into consideration the crystallization during the cooling phase [34] [35]. More recently, Jiang *et al*. [36] estimated the temperature dependent thermal conductivity in transient heat conduction problems. In addition, Zhou *et al*. [37] introduced two methods capable of identifying the temperature dependent thermal conductivity without previously knowing its variation form. Thermophysical characterization through inverse heat conduction problems is achieved on several types of materials. As a matter of fact, the conductivity evolutions of thermal insulation materials under large temperature differences are obtained by solving the uni-directional inverse heat conduction problem [38]. On top of that, the thermal conductivity and specific heat of metallic materials were also identified as a function of temperature [39].

Phase change materials have also been the interest of several studies aiming to characterize their thermophysical properties at their possible states and transitions taking place during their utilization. On one hand, the thermal conductivity of phase change materials, in their solid and liquid states, were simultaneously identified by using a line-source solution for a one-dimensional problem with cylindrical symmetry [40]. The authors have also focused on the unsuccessful estimation of the thermal diffusivities in the solid and liquid states due to their extremely low sensitivities. On the other hand, Courtois *et al*. [41] applied an inverse heat analysis to estimate the effective heat capacity and thermal conductivity of phase change material based on heat flux measurements. The first step of the inverse method consisted in identifying the constant properties in the solid and liquid states, then the melting temperature and the latent heat of fusion were calculated. Nonetheless, the evolutions of the thermophysical properties during the phase change were considered as a mixture between the solid and liquid phases. It was found that additional heat flux measurements within the material are needed to produce better results. Additionally, Zhou *et al*. [42] tested different

discretization schemes to estimate the temperature-dependent thermal conductivity of a phase change material in its solid and liquid phases. The Monte Carlo method was adopted and the discretization scheme requiring the temperature evolution at only one point at the material's surface was the best choice for the inverse method.

The present article focuses on the development of an inverse method capable of identifying the variation of thermal conductivity as a function of temperature and relative crystallinity. The novelty of this research lies in the lack of any prior methodology developed to estimate the evolution of the thermal conductivity function of two coupled fields, without imposing a predefined variation model. The established inverse method contributes in estimating the thermal conductivity profile of a thermoplastic during its crystallization. A numerical model describing the temperature evolution coupled with the crystallization is developed using the Crank-Nicholson scheme. The parameters implemented in the numerical model as well as the boundary conditions are based on experimental measurements and characterizations performed on a polypropylene sample. In this manner, the characterization method is ought to be adequate for real experimental applications. A hybrid optimization algorithm combining a stochastic method with a deterministic one is adopted to take into account the non-linearity and the complexity of the problem. The robustness of the identification method is validated by taking into account the measurement noise and its reliability is perceived by considering the uncertainties of the thermal problem measured parameters. A sensitivity analysis is performed to investigate the accuracy of the results and possible improvements of the estimation method.

2. Numerical Model

The identification method proposed in this study is based on a one-dimensional numerical heat transfer model that takes into account the transition and temperature dependencies of thermal properties. This model describes the transient heat conduction within a polymer, a polypropylene sample that undergoes a phase change during a cooling process.

2.1. Description and resolution of the numerical model

A numerical resolution of the thermal problem is considered for the inverse method. The numerical direct model corresponds to the cooling of a thermoplastic, with a predefined thickness e, from its molten state by imposing a temperature variation on its upper and lower surfaces. A schematic representation of the measurement point within the polymer and the imposed boundary conditions is shown in Figure 1. The polymer undergoes a phase change, during its cooling, corresponding to the germination and the growth of crystals. The crystallization kinetics, basically described by the theory of Nakamura [43] [44], is strongly dependent on the temperature variation. Furthermore, the thermophysical properties vary with temperature and relative crystallinity α, describing the evolution of the crystallization process. The one dimensional heat equation modelling the thermal response of the polymer is coupled with the exothermal heat generation taking place during the crystallization phase. The coupled heat conduction problem is described by equations 1 and 2:

$$\rho(\alpha,T)C_p(\alpha,T)\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda(\alpha,t)\frac{\partial T}{\partial x}\right) + \rho(\alpha,T)\Delta H\frac{\partial \alpha}{\partial t} \quad \forall x \in]0;e[\;\; \forall t > 0 \tag{1}$$

$$\frac{\partial \alpha}{\partial t} = n \times K_{Nak}(T) \times (1-\alpha)[-ln(1-\alpha)]^{1-\frac{1}{n}} \quad \forall x \in [0;e] \;\; \forall t > 0 \tag{2}$$

With ΔH being the crystallization enthalpy, $K_{Nak}(T)$ the Nakamura coefficient function of temperature and n the exponent of Avrami [45] [46] [47]. The traditional differential form of Nakamura [43] [44] is reduced to an equation that is easier to apply and solve numerically. Levy [48] proved the robustness and the accuracy of writing the crystallization kinetic in the following form:

$$\frac{\partial \alpha}{\partial t} = K_{Nak}(T).G(\alpha) \;\; \forall x \in [0;e] \;\; \forall t > 0 \tag{3}$$

With $G(\alpha)$ a function computed over the interval [0,1].
A Dirichlet boundary condition is applied on both edges and is written as:

$$T(x=0,t) = T_1(t) \;\; \forall t > 0 \tag{4}$$

$$T(x = e, t) = T_2(t) \quad \forall t > 0 \tag{5}$$

The initial conditions of the thermal problem are:

$$T(x, t = 0) = T_{Initial} \quad \forall\ x \in [0; e] \tag{6}$$

$$\alpha(x, t = 0) = 0 \quad \forall\ x \in [0; e] \tag{7}$$

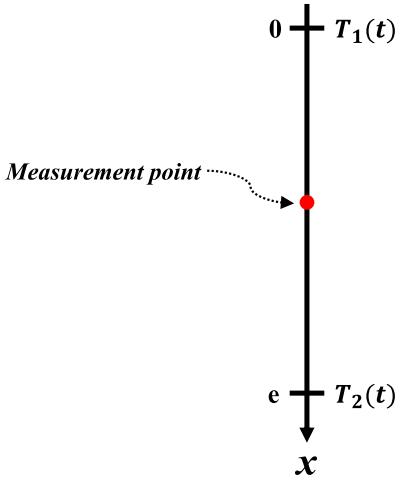


Figure 1: Physical configuration of the thermal problem, and boundary conditions along with the measurement point

The specific heat capacity, the density and the thermal conductivity are described by equations 8, 9 and 10, where "sc" and "a" refer to the semi-crystalline and amorphous phases respectively.

$$C_p(T, \alpha) = C_{p_{sc}}(T) \times \alpha + C_{p_a}(T) \times (1 - \alpha) \tag{8}$$

$$\rho(T, \alpha) = \rho_{sc}(T) \times \alpha + \rho_a(T) \times (1 - \alpha) \tag{9}$$

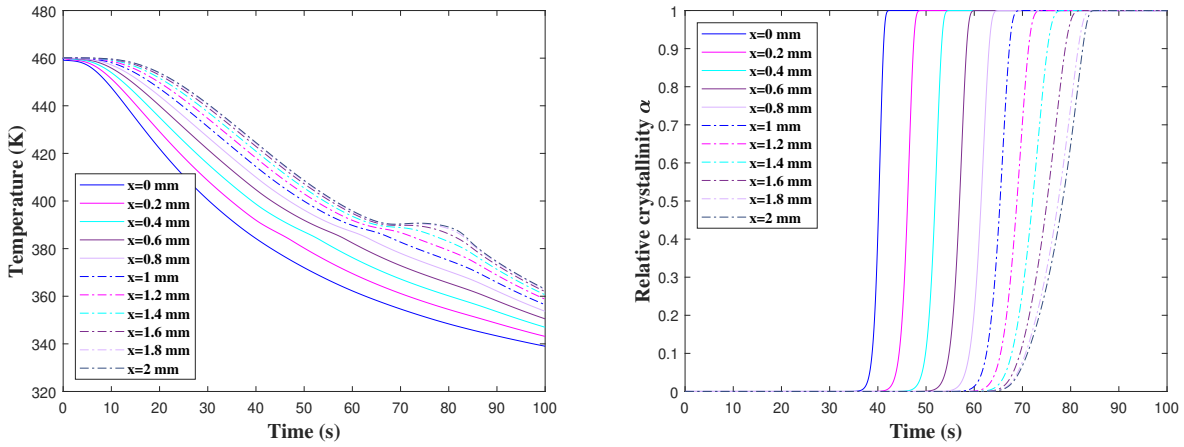
$$\lambda(T, \alpha) = \lambda_{sc}(T) \times \alpha + \lambda_a(T) \times (1 - \alpha) \tag{10}$$

The temperature dependent specific volume is measured with the help of a home made PVT device [49]. The specific heat as well as the crystallization kinetics is determined by differential scanning calorimetry (Q200, TA instruments). The experimental protocols applied are described in details by le Mouellic [50].

The heat transfer problem is modelled using the finite difference method. The Crank-Nicolson scheme is adopted to discretize the one dimensional heat problem. The resolution of the numerical problem is achieved through iterative calculations as explained in a previous study [51].

An example of the results generated by the numerical model is represented in Figures 2a and 2b. The cooling of polypropylene from an initial temperature of 460 K is simulated. The temperature applied at both extremities decreases in time at a cooling rate of 1.2 K/s. The temperature and the relative crystallinity evolutions at different positions of the material's thickness are then obtained. Since the boundary conditions at both extremities are similar and the polymer is isotropic, the thermal problem is symmetric. In this case, the results plotted correspond to the evolutionary profiles calculated at different positions located between the edge and $\frac{e}{2}$. An evaluation of the model is

performed by comparing its results with an analytic model, in pure conduction, and with the commercial software Comsol Multiphysics, while taking into consideration the crystallization. These comparisons assisted in verifying the precision of the model and its reliability to proceed with the inverse method [51].



(a) (b)

Figure 2: Outputs of the numerical model: (a) Temperature evolution and (b) Relative crystallinity evolution (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article)

2.2. *Sensitivity to the thermophysical properties*

It is essential to note how sensitive the model outputs are to the unknown parameters before attempting to determine the desired thermophysical properties. This analysis is required to verify the feasibility of the estimation and to acknowledge for the possible existing correlations among the properties. The sensitivity coefficient $S_j(t,\beta_j)$ is defined as the first derivative of the system's output with respect to the parameter β_j. It is similar to observing the effect of small perturbation $\delta\beta_j$ on the thermal response. However, in order to ensure a proper comparison of the impact of different thermophysical properties, the sensitivity coefficients must have similar units [52] [53]. Hence, the temperature reduced sensitivity with respect to the thermal conductivity λ, specific heat C_p and density ρ is computed. It is defined as:

$$S_j^*(t,\beta_j) = \frac{\partial Y(t,\beta_j)}{\partial \beta_j} \times \beta_j = \lim_{\delta\beta_j \to 0} \frac{Y(t,\beta_j + \delta\beta_j) - Y(t,\beta_j)}{\delta\beta_j} \times \beta_j \tag{11}$$

With β being the set of parameters to identify and Y the output of the system.

The obtained results are plotted in Figure 3. The similar variations of the sensitivities curves during the overall exploitation time demonstrate the correlations between the thermophysical properties. In this case, the alteration of the model output can be related to any parameter of the thermal problem.

Assuming that the measurement errors are additive and have a constant standard deviation, the covariance matrix is calculated based on the sensitivity matrix S. It is defined by the following equation:

$$Cov(\beta) = \sigma^2 (S^T S)^{-1} = \begin{pmatrix} \sigma^2_{\beta_1} & Cov(\beta_1,\beta_2) \\ Cov(\beta_1,\beta_2) & \sigma^2_{\beta_2} \end{pmatrix} \tag{12}$$

where σ is the standard deviation of the measurement noise.
The diagonal terms of the covariance matrix correspond to the variance $\sigma^2_{\beta_j}$ of each of the unknown parameters. The covariance between the parameters is defined and assessed by the non-diagonal terms [54]. The correlation coefficient r between two parameters is then computed by the following equation:

$$r = \frac{Cov(\beta_1,\beta_2)}{\sigma_{\beta_1}\sigma_{\beta_2}} \tag{13}$$

The correlation matrix of the three thermophysical properties has been calculated as shown in Equation 14. It appears more clearly that the thermal conductivity and the specific heat are highly correlated since their correlation coefficient is close to 1. This ascertainment may define the inverse problem as ill-posed preventing the simultaneous identification of the parameters [55]. Consequently, the study will be conducted towards identifying only the thermal conductivity of the polymer as a function of the temperature and the relative crystallinity.

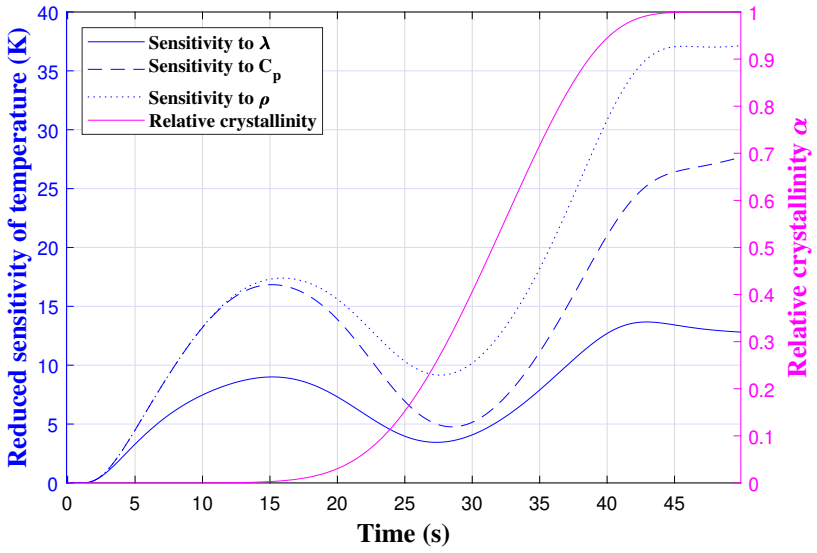


Figure 3: Reduced sensitivity of the temperature with respect to the thermophysical properties

$$cor(\lambda,\rho,C_p) = \begin{pmatrix} \lambda & \rho & C_p & \\ 1 & -0.1883 & 0.9609 & \lambda \\ & 1 & -0.4458 & \rho \\ & & 1 & C_p \end{pmatrix} \tag{14}$$

3. Inverse problem and estimation strategy

This part is dedicated to the detailed description of the inverse strategy leading to the identification of the thermal conductivity function of temperature and relative crystallinity. This section primarily covers the set of parameters to be identified, the sensitivity analysis, the optimization algorithm, and an explanation of the inverse method. The established method is validated with the help of generated synthetic data.

3.1. Unknowns of the inverse heat conduction problem

According to the sensitivity analysis, the inverse technique is applied to estimate the thermal conductivity while the other parameters are supposed to be known. The specific heat capacity and the density are implemented as described in Equations 8 and 9. The inverse problem treated here is rather complex since the evolution of the thermal conductivity, dependent on two coupled fields, is estimated. The conductivity values corresponding to the possible combinations of temperature and relative crystallinity are stocked in the following matrix:

$$\begin{bmatrix} T_1 & T_2 & T_3 & \dots & \dots & \dots & \dots & \dots & T_n \end{bmatrix} \tag{15}$$

$$\begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_m \end{bmatrix} \begin{pmatrix} \lambda_{11} & \lambda_{12} & \dots & \dots & \dots & \dots & \dots & \lambda_{1n} \\ \lambda_{21} & \lambda_{22} & \dots & \dots & \dots & \dots & \lambda_{2n-1} & \lambda_{2n} \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \vdots & \vdots \\ \lambda_{m1} & \lambda_{m2} & \dots & \dots & \dots & \dots & \lambda_{mn-1} & \lambda_{mn} \end{pmatrix} \tag{16}$$

This matrix is defined by n levels of temperature and m levels of relative crystallinity and will assist in estimating the thermal conductivity of the polymer during its crystallization. The selected n temperature levels cover the entire crystallization domain. Also, the m relative crystallinity levels delimit the transformation phase: $\alpha_1 = 0$ and $\alpha_m = 1$. For a certain combination of temperatures and relative crystallinities, the thermal conductivity is calculated by performing a double linear interpolation function of T and α.

However, the relative crystallinity of the polymer is fixed in both the molten and solid states: $\alpha = 0$ and $\alpha = 1$ respectively. Therefore, the thermal conductivity of the molten or solid polymer is only dependent on the temperature. The conductivity of the liquid polymer is defined as a set of values corresponding to the possible k temperature levels:

$$\begin{pmatrix} \lambda_{l1} & \lambda_{l2} & \dots & \dots & \dots & \dots & \dots & \lambda_{lk} \end{pmatrix} \tag{17}$$

Similarly, the solid polymer's thermal conductivity function of temperature levels p is assigned a different set:

$$\begin{pmatrix} \lambda_{s1} & \lambda_{s2} & \dots & \dots & \dots & \dots & \dots & \lambda_{sp} \end{pmatrix} \tag{18}$$

In this manner, the thermal conductivity in the molten and solid states is calculated by a linear interpolation-only function of temperature. One should note that the temperature domains corresponding to each of the three possible states (solid, liquid and during crystallization) depend chiefly on the cooling rate. Indeed, the onset crystallization temperature increases with the slower cooling rates and vice versa [56].

3.2. Sensitivity analysis and conditioning of the inverse problem

As previously mentioned, the crystallization domain is highly dependent on the cooling rate [56]. Hence, specifying the temperature range of the matrix 15 relies mainly on the physical thermal problem. Additionally, one must note that the thermal conductivity matrix cannot be entirely estimated by the inverse heat conduction problem, based on a single cooling rate experiment. The relative crystallinities α, ranging between 0 and 1, are associated with temperature levels according to the crystallization kinetic [43] [44]. Actually, the thermal conductivities that can be accurately identified are the ones that are involved in the polymer's thermal response calculations. Some parameters of the matrix have indeed no influence on the model output and their inclusion may define the problem as being ill-posed. However, their incorporation is a must to map entirely the implemented thermal conductivity matrix.

A sensitivity study is achieved to investigate the temperature sensitivity to the elements of the thermal conductivity matrix. This case study is achieved for an average cooling rate of 15.2 K/min at the center of the polymer. The reduced temperature sensitivities with respect to all the parameters of the thermal conductivity matrix are calculated and the most temperature-sensitive parameters are selected (Figure 4). For clarity reasons, the thermal conductivity coefficients with the associated levels of temperature and relative crystallinity are presented in Table 1. According to the previous kinetic measurements of crystallization performed on a polypropylene sample, the crystallization starts at a temperature of 402 K and ends around 398 K. As expected, the temperature at the center of the polymer is sensitive to the thermal conductivities corresponding to this temperature interval.

Table 1: Temperature and relative crystallinity levels of the identifiable thermal conductivities

α / T (K)	396	398	400	402	404
0				λ_1	λ_2
0.2			λ_3	λ_4	
0.4			λ_5	λ_6	
0.6			λ_7	λ_8	
0.8		λ_9	λ_{10}		
1	λ_{11}	λ_{12}			

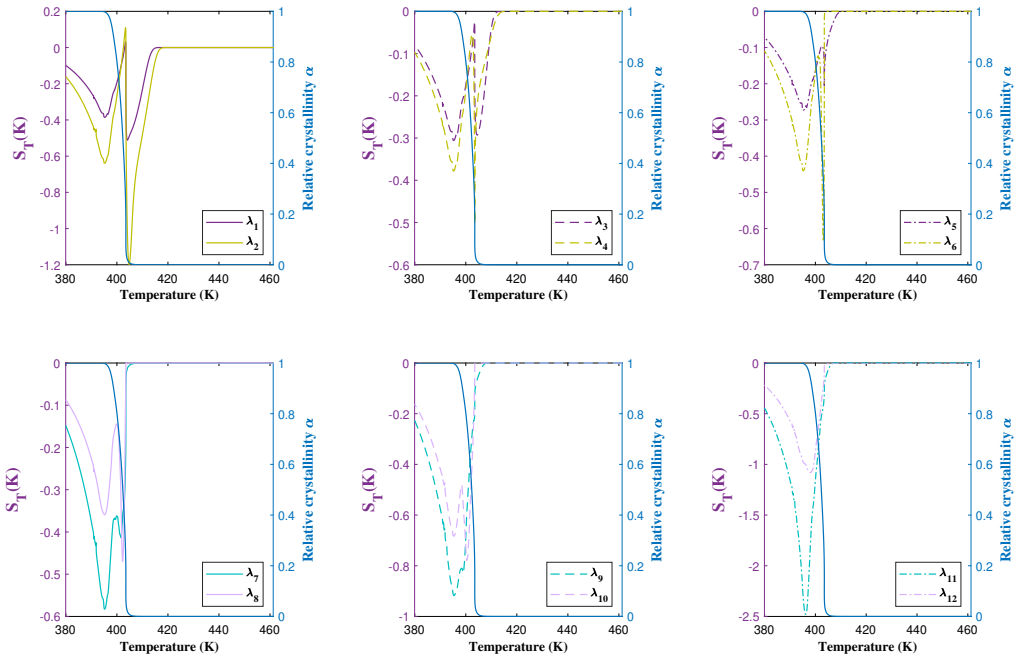


Figure 4: Temperature Reduced sensitivity with respect to the thermal conductivities of the crystallization phase

The sensitivity curves seem to have similar shapes which may reveal a correlation among the parameters in question. The correlation matrix is computed (Equation 19) and the thermal conductivities λ_4 and λ_5 appear to be strongly correlated since their correlation coefficient is -0.94. λ_7 and λ_8 as well as λ_7 and λ_{10} seem to also have a correlation coefficient close to 0.86.

$$cor = \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda_3 & \lambda_4 & \lambda_5 & \lambda_6 & \lambda_7 & \lambda_8 & \lambda_9 & \lambda_{10} & \lambda_{11} & \lambda_{12} \\ 1 & -0.58 & -0.57 & -0.43 & 0.33 & -0.11 & 0.34 & -0.38 & -0.16 & -0.29 & -0.16 & 0.14 \\ & 1 & -0.28 & -0.14 & 0.31 & 0.017 & -0.11 & 0.07 & -0.09 & 0.08 & 0.03 & 0.06 \\ & & 1 & 0.51 & -0.61 & 0.01 & -0.09 & 0.18 & 0.16 & 0.09 & 0.08 & -0.11 \\ & & & 1 & -0.94 & 0.30 & -0.58 & 0.74 & 0.49 & 0.54 & 0.25 & -0.36 \\ & & & & 1 & -0.19 & 0.40 & -0.60 & -0.54 & -0.39 & -0.15 & 0.39 \\ & & & & & 1 & -0.79 & 0.48 & 0.29 & 0.75 & 0.32 & -0.33 \\ & & & & & & 1 & -0.86 & -0.55 & -0.86 & -0.33 & 0.51 \\ & & & & & & & 1 & 0.61 & 0.63 & 0.20 & -0.45 \\ & & & & & & & & 1 & 0.41 & -0.27 & -0.78 \\ & & & & & & & & & 1 & 0.50 & -0.62 \\ & & & & & & & & & & 1 & -0.18 \\ & & & & & & & & & & & 1 \end{pmatrix} \quad (19)$$

The sensitivity analysis is completed by evaluating the relative error of each parameter to be identified by considering a constant standard deviation of the noise σ [54]:

$$re(\lambda_i) = \frac{\sigma}{\lambda_i} \sqrt{diag(S_i^t S_i)^{-1}} \quad (20)$$

The calculated relative errors are presented in Table 2. Despite the existing correlation among some of the unknown parameters, it is possible to identify the thermal conductivity values during the crystallization of polypropylene at temperatures ranging between 398 and 402 K. Indeed, the computed relative errors are reasonable and do not exceed 11%.

Table 2: Relative errors of the thermal conductivity coefficients

λ	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7	λ_8	λ_9	λ_{10}	λ_{11}	λ_{12}
Relative error (%)	2.67	0.98	4.20	4.21	10.75	1.26	6.77	3.22	4.02	2.67	0.77	2.32

The thermal conductivities of the amorphous and semi-crystalline states affect also the temperature evolution of the polymer and may be identified within an acceptable precision range. The corresponding sensitivity curves and correlation matrices are not presented in this paper since this analysis has been exhaustively achieved in previous researches [34] [35]. Rather, the liquid-to-solid phase transition is the main topic of the current study.

The sensitivity study has revealed possible correlations among the thermal conductivities additionally to the fact that the inverse problem is overparametrized. The degrees of freedom of the problem is ought to be tracked through statistical tools revealing hidden correlations among the unknowns and the feasibility of the estimation. Indeed, the condition number of the matrix $S^{*T}S^*$ may answer the question of the identifiability of the parameters [53]. It is defined by the following equation:

$$Cond(S^{*T}S^*) = \frac{\xi_{max}(S^{*T}S^*)}{\xi_{min}(S^{*T}S^*)} \quad (21)$$

Where $\xi_{max}(S^{*T}S^*)$ is the highest eigen value of the information matrix $S^{*T}S^*$, known also as Fisher matrix, and $\xi_{min}(S^{*T}S^*)$ is the lowest eigen value.
If correlation exists between the sensitivity coefficients, the inversion of the matrix $S^{*T}S^*$ amplifies the synthetic noise due to the presence of singularities. The condition number will then take high values. When including all the thermal conductivities of the matrix 15, the condition number tends towards infinity. When just the twelve parameters of Table 1 are taken into account, the condition number is greatly lowered, improving the inverse problem's ability to be solved.

3.3. Optimization algorithm

The identification of the thermal conductivity values can be achieved by applying a stochastic optimization algorithm or a deterministic one. Since the actual problem is non-linear and presents a relatively high number of

parameters, the use of a stochastic approach is required to avoid getting trapped in a local minimum. Among the stochastic approaches, the metaheuristic techniques are nature inspired and zero-order algorithms. In a previous study, the aptitudes of the Particle Swarm Optimization algorithm (PSO) [57] and the Genetic Algorithm (GA) [58] [59] for identifying the unknown parameters were tested [51]. The stochastic algorithm (PSO or GA) was combined with a deterministic method. The final estimation values optimized by the stochastic technique were implemented as initial values to the gradient-based algorithm. The interior point algorithm able to solve non-linear convex problems, was adopted [60]. It was found that the results obtained by the Genetic Algorithm are more accurate than the values found by the Particle Swarm Optimization Algorithm. Therefore, the Genetic Algorithm coupled with the interior point method is adopted in this case study. The strategy of combining a stochastic approach with a deterministic one takes advantage of both methods. Indeed, the metaheuristic algorithms are able to search for the global minimum region and the interior point method converges towards the local optimum in this region. By providing the initial guess from the stochastic algorithm, the interior point method converges towards satisfactory results.

3.3.1. Genetic algorithm

The genetic algorithm is one of the first stochastic optimization algorithms inspired from the behavior and the evolution of populations. It relies on the simulation of species individuals tending to go through mutation according to their survival instinct. The logic behind this principle reflects mainly Darwin's theory of evolution [59] [61]. Each chromosome represents a solution and each gene corresponds to one of the parameters to identify. The potential of each individual is evaluated by the objective function. The random selection of the optimal solutions is achieved by the roulette mechanism, where the probability of adopting a solution is inversely proportional to the value of its cost function. The main interest of the genetic algorithm resides in the fact that it preserves the best individuals of each generation in order to enhance the other solutions. This method is constituted of four steps consisting in creating the initial population, selecting the best individuals based on their potentials, combining the individuals to create a new generation and mutating some individuals to avoid getting trapped in a local minimum.

The genetic algorithm has been extensively used in several domains and has proved its ability to solve complex problems with linear and non-linear constraints. Several inverse heat conduction problems have been solved with the help of the genetic algorithm [62] [63] [64]. It is capable of leading the population towards the optimal solution without requiring exhaustive informations about the problem.

3.3.2. Interior point method

The interior point method is well adapted for solving linear and non-linear convex optimization problems. This algorithm excels the simplex algorithm that was traditionally used in linear optimization [65]. Its detailed mathematical implementation in computer calculation is provided by Byrd *et al*. [66]. Since the problem is subjected to constraints, the method of Lagrange is applied [67] [68]. The problem is solved using Newton's method while the conjugate gradient method is used when the problem is not locally convex. The conjugate gradient method is a first-order algorithm, powerful for solving linear and non-linear inverse problems, while Newton's method is a second-order algorithm. It requires the inversion of the Hessian matrix which may be singular due to the overparametrized problem. By enhancing the approximation of the Hessian matrix and its inverse, the BFGS algorithm overcomes the restriction of the Hessian to be positive definite [69] [70] [71] [72].

3.4. Presentation of the cost function

The ultimate aim of the current inverse method for thermal conductivity estimation is optimization. The resolution of the inverse problem relies on minimizing an objective function representing the discrepancy between the experimental or synthetic results and the numerical results. The optimization algorithm keeps on adjusting the values of the thermal conductivity until the cost function satisfies a predefined criterion. The cost function is described by the following formula:

$$J = \sqrt{\frac{\sum_{i=1}^{n} \int_0^{t_f} (T_{i,Experimental}(\lambda) - T_{i,Numerical}(\lambda))^2 dt}{n \times t_f}} \tag{22}$$

With n being the number of points where the temperature variation is measured or computed, t_f the experiment time length and λ the set of thermophysical properties to identify. For this case study, $T_{i,Numerical}$ refers to the temperature variation computed by the developed numerical model (Section 2).

It is considered that the temperature field is measured at the center of the polymer since the crystallization is mostly detected at this point (Figure 2a). Synthetic signals are generated with the help of the numerical model to assess the performance of the proposed estimation algorithms. To obtain experimentally accurate temperature evolutions, the boundary conditions imposed at the front and rear faces have been recorded with the help of an instrumented mold developed by the LTEN laboratory. The main purpose of this experimental apparatus was to record the temperature variations within a material and on its edges during heating and cooling cycles. The thermal problem is asymmetric since the temperature variations at the front face $T_1(t)$ and at the rear face $T_2(t)$ are not similar due to different cooling modes imposed. The cooling of a polypropylene from its melted state is then simulated by implementing its volumetric heat capacity $\rho C_p(\alpha, T)$, its crystallization kinetic $K_{Nak}(T)$ and the boundary conditions $T_1(t)$ and $T_2(t)$. A uniform initial temperature of 460 K, greater than the melting point of the polypropylene ($\approx$ 440 K), is considered. In this manner, the crystallization of the polymer is ought to take place during its cooling. The polymer is therefore initially in its molten state with a relative crystallinity $\alpha = 0$. The relative crystallinity α will progressively increase during its crystallization before reaching a final value of $\alpha = 1$ corresponding to the solid state. Hence, the three distinct phases of the polymer's thermal conductivity can be determined using synthetic data.

4. Estimation results

In this section, the results obtained by different estimation strategies are presented and analyzed in order to observe the different aspects related to the applied inverse method. A matrix of temperature and transformation dependent thermal conductivities is estimated using synthetic data generated by the numerical model. The conventional mixing law is used to obtain the values of the thermal conductivities that are used in this model. The potential of the optimization algorithm in estimating the thermal conductivity values, corresponding to the different combinations of temperature and relative crystallinity levels, is evaluated.

4.1. Estimation without noise

As mentioned in Section 3.3, the identification calculation is conducted using the genetic algorithm coupled with the interior point method. In this case, only the temperature evolution recorded by the thermocouple at the center (Figure 1) will be considered to compute the cost function. Each generation of the genetic algorithm is constituted of 20 individuals, the cross-over among the individuals is achieved through the cross-over heuristic function with a ratio of 1.2 and the cross-over fraction is set to 0.8 [73] [74]. The lower and the upper bound of the thermal conductivity are set to 0.1 and 0.3 respectively. Firstly, the importance of using a hybrid optimization algorithm is highlighted by comparing its results with the ones obtained with the help of the genetic algorithm alone.

According to the generated numerical signals, the crystallization occurs at temperatures ranging between 392 and 418 K. This wide range is explained by the temperature gradient within the polymer's thickness. Indeed, the cooling rate varies along the thickness leading to different crystallization evolutions. In this context, the thermal conductivity values, within this temperature range, are stocked in a matrix (Equation 15) with a relative crystallinity increment of $\delta\alpha = 0.2$ and a temperature increment of $\delta T = 2$ K. The amorphous state ($\alpha = 0$) is considered in the temperature range [415 ; 455] K and the solid state ($\alpha = 1$) in the range [345 ; 395] K. It is reminded that these temperature ranges are selected according to the outputs of the numerical model, as represented in Figures 2a and 2b. The observed temperature plateau corresponds to the exothermal heat released during crystallization whose kinetic has been determined by differential scanning calorimetry (Section 2.1). The temperature increment in the amorphous and solid states is set to $\delta T = 10$ K. A minor temperature difference is utilized during the crystallization to ensure the precision of the results. Indeed, crystallization can occur within a limited temperature range at a specific thickness point.

The identified thermal conductivity values are compared with the original ones issued from the mixing rule (Equation 10) and used to produce the synthetic results. The results proved that the hybrid optimization algorithm is capable of resolving the complex and non-linear inverse problem with a higher accuracy than the stochastic method. It was demonstrated that the genetic algorithm in conjunction with the interior point method could identify the thermal conductivity coefficients with an error of no more than 2%, whereas the relative errors linked to the genetic algorithm actually range between -10 and 5 %. Using the numerical simulation with the identified values of the thermal conductivity, the temperature and relative crystallinity evolutions at different positions of the thickness are obtained. A

double linear interpolation function of T and α is then performed to compute the corresponding values of thermal conductivity. Consequently, the effective thermal conductivity function of the two coupled fields is obtained at all the discretized points.

As matter of fact, not all the unknown values can be identified accurately but some are used as intermediate values to ensure the convergence of the iterative calculation. The "original" thermal conductivity values are simply calculated by the adopted mixing law using the synthetic signals of T and α. The comparisons between the "original" thermal conductivity values and the values estimated using the genetic algorithm and the hybrid optimization algorithm are represented in Figures 5 and 6 respectively. The thermal conductivity evolution function of relative crystallinity is plotted at different positions of the thickness based on the results of the hybrid optimization algorithm (Figure 7). For clarity reasons, the thermal conductivity profiles at 12 nodes, out of 36 in total are illustrated. The reliability and validity of the hybrid optimization algorithm is once again proven since the relative difference is less than ±2% at the different positions.

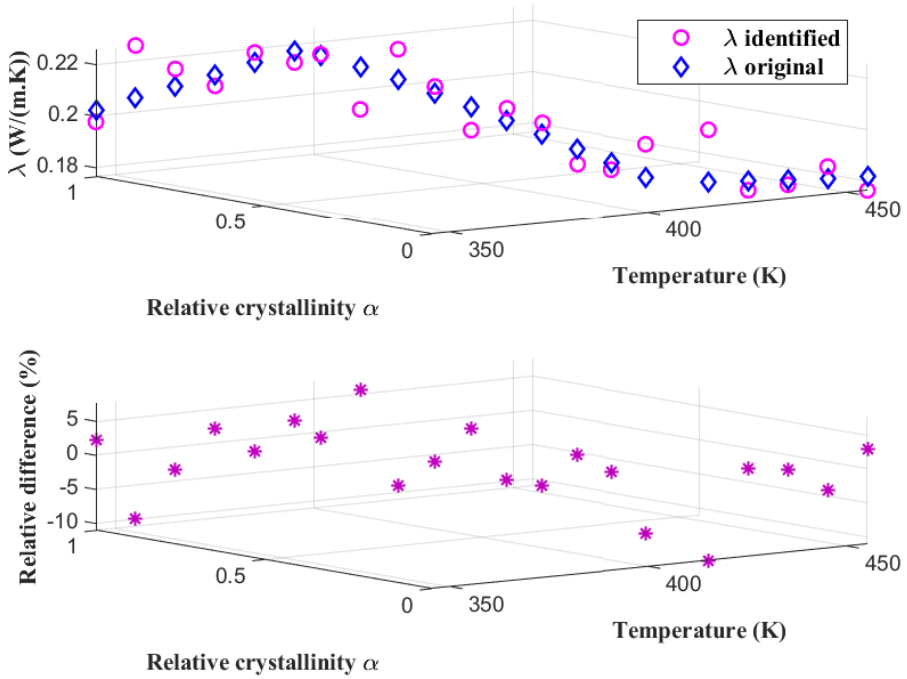


Figure 5: Comparison between the "original" values of the thermal conductivity and the values estimated by the genetic algorithm, without synthetic noise

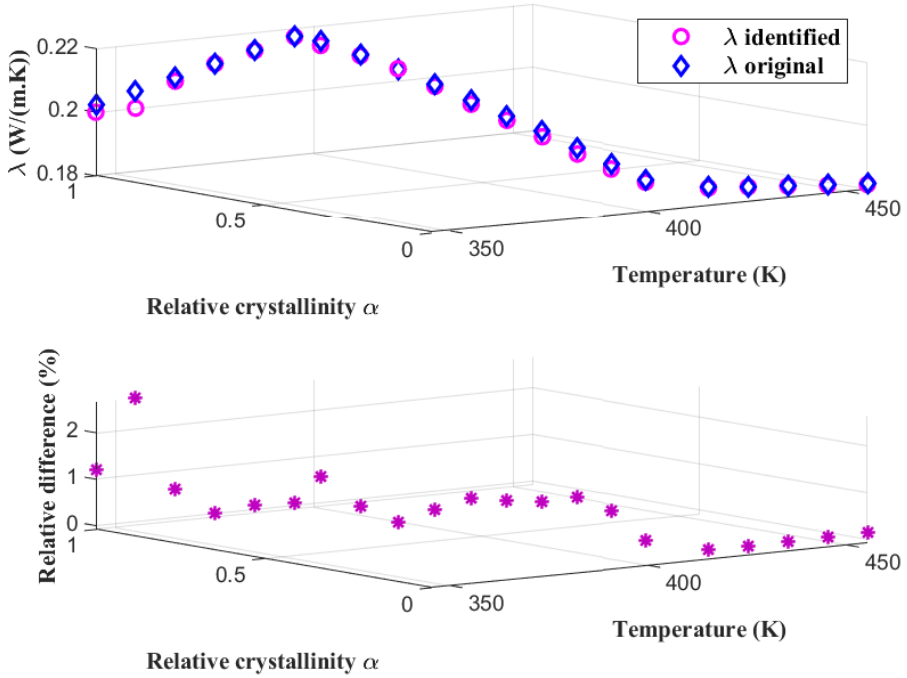


Figure 6: Comparison between the ”original” values of the thermal conductivity and the values estimated by the hybrid optimization algorithm

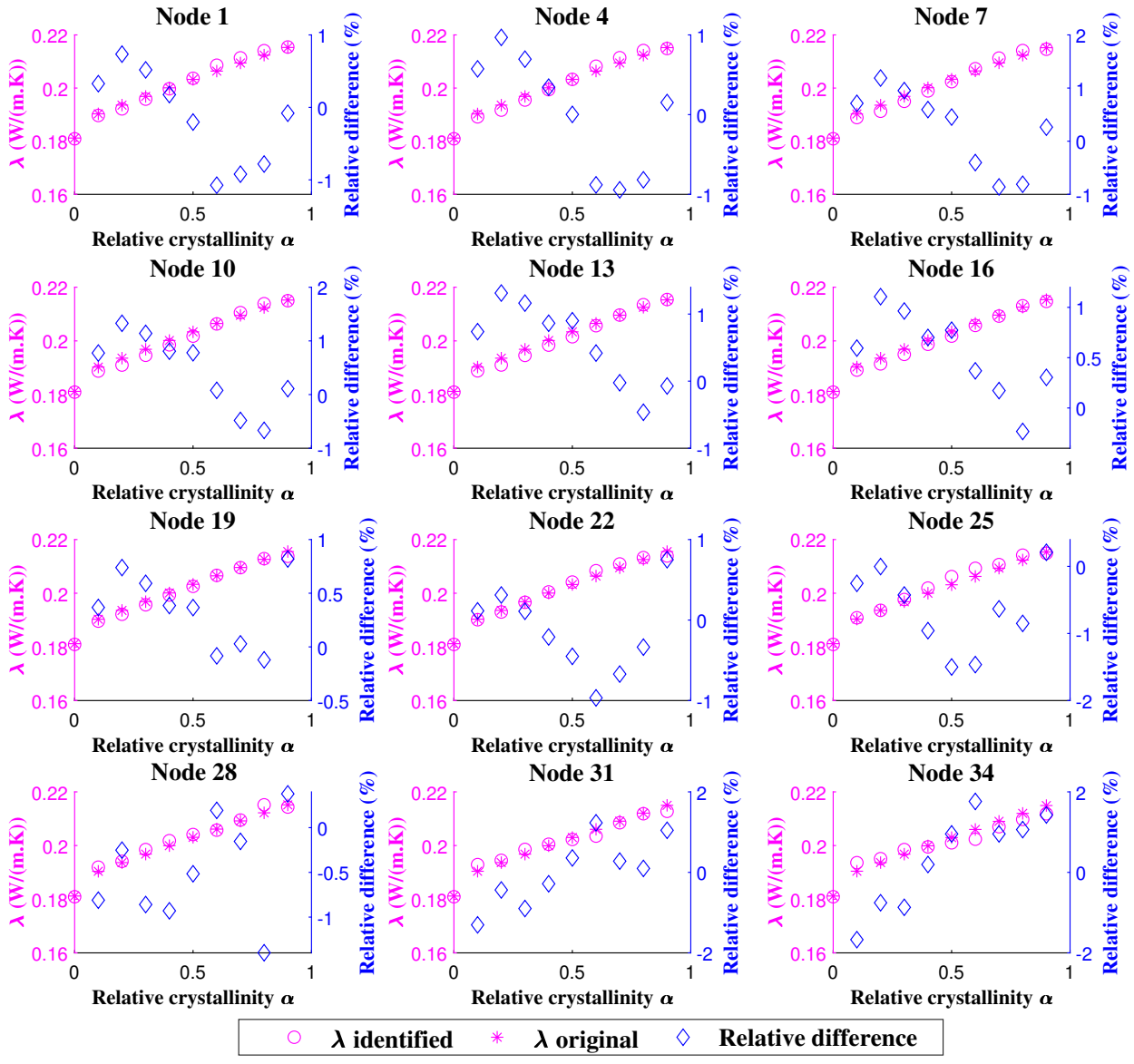


Figure 7: Comparison between the "original" values of the thermal conductivity and the values estimated by the hybrid optimization algorithm on several nodes of the thickness

Furthermore, the temperature residuals are shown in Figures 8a and 8b. A close agreement between the temperature profiles is observed. However, the temperature residuals corresponding to the results of the hybrid algorithm are 100 times smaller than the residuals of the stochastic algorithm. Thus, it is concluded that the deterministic algorithm, succeeding the stochastic one, is crucial to converge towards the optimal solution of the thermal problem. Indeed, the stochastic aspect of the genetic algorithm handles the complexity and the great number of unknowns to provide an initial guess to the deterministic method. The interior point algorithm is then capable of finding the local minimum in the global minimum region while handling the overparametrized problem.

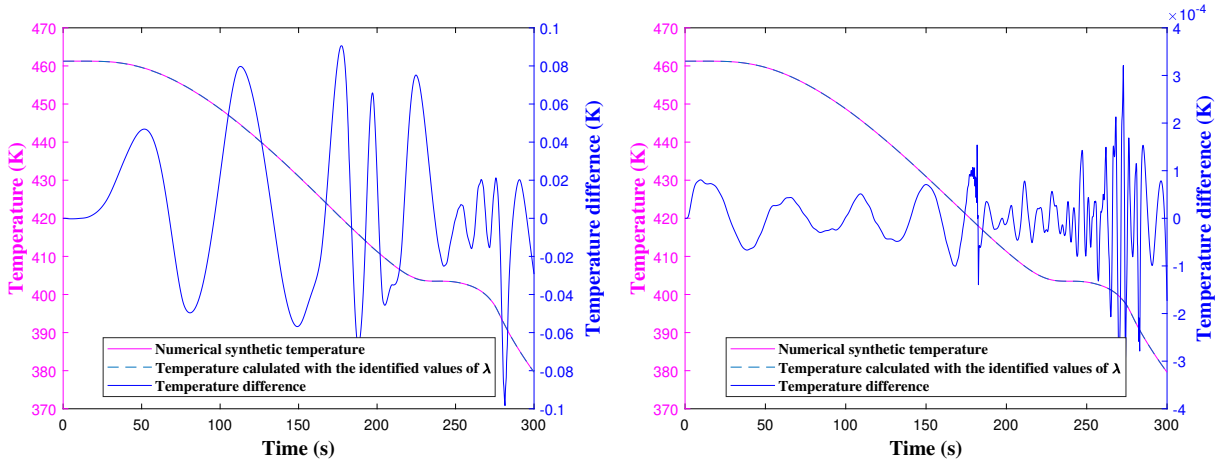


Figure 8: Temperature residual between the original temperature profile and the profile computed using the values identified, without synthetic noise, by (a) GA alone and (b) GA coupled with the interior point method

4.2. Estimation with noise and uncertainties

In this section, the identification technique is applied while taking into account the measurement noise as well as the possible uncertainties of the thermal problem parameters. The purpose behind this analysis is to test the reliability of the inverse method when being applied with practical measurements. For this manner, the calculations are run when the data are corrupted by noise, the thermocouple position is inexact and a percent error is added to the experimentally identified parameters (such as ρ, C_p, ΔH and K_{Nak}).

4.2.1. Estimation with noise

The robustness of the identification method is firstly tested by adding a random noise to the numerical temperature evolution. This approach is considered to evaluate the effect of the measurement noise on the identification strategy. A random number generator is used to create the noisy signal, and it follows a Gaussian distribution that is parameterized according to the desired noise level. Figures 9 shows the relative differences of the estimated values of the thermal conductivity with a standard deviation of $0.025°C$, which is representative of the experimental noise. The percent error remains acceptable as it does not exceed 5% and the linear evolution of the thermal conductivity is conserved. For further validation, the identification is repeated with a standard deviation noise of $0.05°C$ for which the relative difference reaches a maximum of 10%. The temperature residuals corresponding to the identified thermal conductivities are calculated (Figures 10a and 10b), and the standard deviations for each of the residuals are respectively $0.0253°C$ and $0.0497°C$. The temperature residuals are found to be well-centered, and their standard deviations remain lower than or equal to the standard deviation noise σ_{Noise}. This ascertainment proves the accuracy and the feasibility of the estimation method.

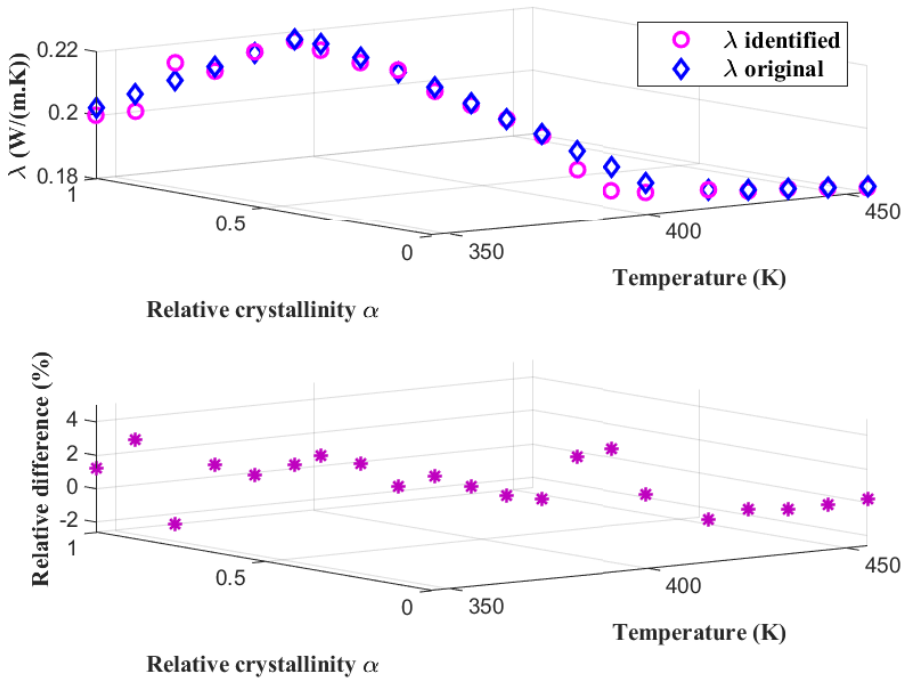


Figure 9: Comparison between the "original" values of the thermal conductivity and the values estimated by the genetic algorithm coupled with the interior point method with a noise of 0.025 $°C$

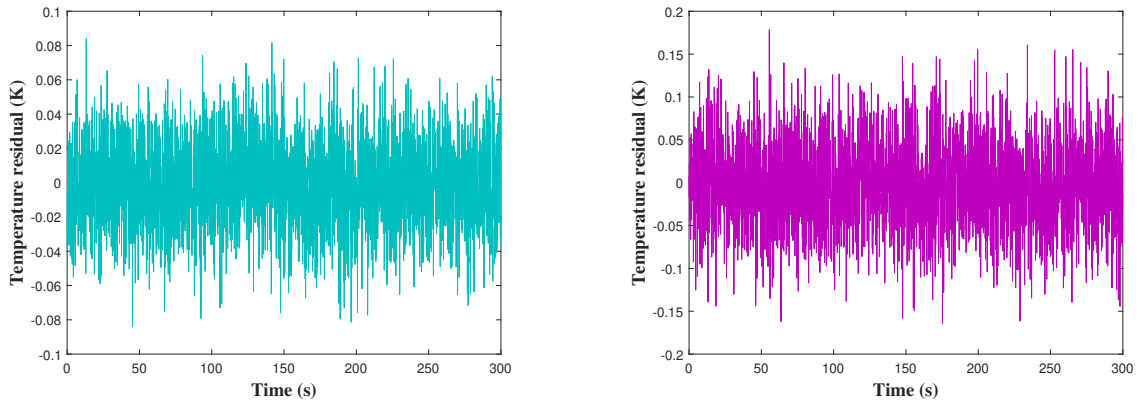


Figure 10: Temperature residual between the original temperature profile and the noisy profile simulated using a noise with a standard deviation of (a) 0.025 $°C$ and (b) 0.05 $°C$

4.2.2. Effect of the material's shrinkage on the identification method

The shrinkage of the molded plastic during its cooling leads to its volume contraction. Hence, the measurement points are not fixed in space and will undergo displacement along the direction of the thickness. Thereby, the shrinkage of the polymer must be taken into account in the numerical model. In this manner, the variation of the polymer's thickness is computed according to the apriori known density $\rho(\alpha, T)$. The section S as well as the mass m are considered to be constant and the thickness dependence of the temperature T and the relative crystallinity α corresponds

to the following formula: $h(T,\alpha) = \frac{m}{S \times \rho(T,\alpha)}$.

The importance of taking into consideration the material's shrinkage is highlighted in this section. In fact, the shrinkage significantly affects the results of the direct simulation as it controls the meshes length and the displacement of the measurement points. To investigate its effect on the identification, an inverse calculation is performed without accounting for shrinkage in the numerical model calculations. Therefore, a uniform and constant discretization of space over time, is considered. The noise intensity added to the synthetic signal is $0.025°C$. The obtained results (Figure 11) exhibit a relative difference of 30% between the thermal conductivity profile and the original one. In this manner, neglecting the polymer's shrinkage has a significant impact on the identification and distorts the thermal conductivity evolution during crystallization.

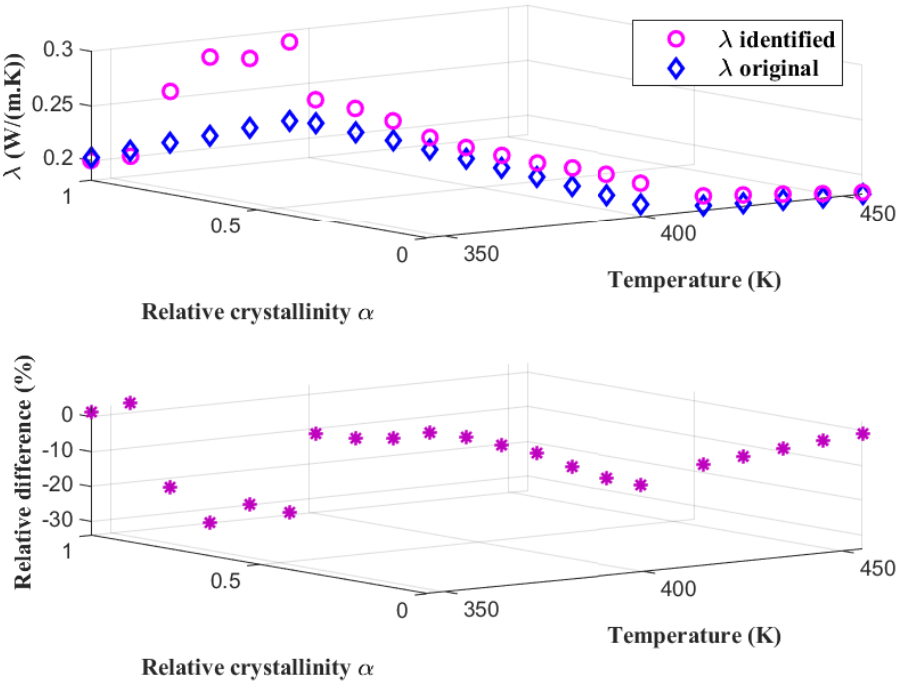


Figure 11: Comparison between the "original" values of the thermal conductivity and the values estimated by the genetic algorithm coupled with the interior point method without taking into account the material's shrinkage, with a noise of $0.025°C$

4.2.3. Effect of the parameters uncertainties on the identification method

Considering the factors that can lead to errors in the estimated thermal conductivities is necessary for an effective evaluation of the inverse technique. In such manner, the impact of the thermal parameters uncertainties is investigated by recognizing the accuracy of the obtained results. The thermal problem parameters are measured or assumed to be known. They are not to be estimated but they can affect the identification process. Any error on these parameters values may result in consequent error on the estimated solution [75]. The inverse calculation is therefore performed while adding an error percentage on the parameters of the direct model. A noise with a standard deviation noise of $0.025°C$ is taken into account in the following calculations.

Firstly, an error of 2% is added to the density $\rho(T,\alpha)$ and the specific heat $C_p(T,\alpha)$. This error reflects the experimental characterization uncertainty. The relative errors of the estimated thermal conductivity values are then computed. It is observed in Figure 12 that the thermal conductivity is identified with an error lower than 4% while conserving the linear evolution of the original profile. Secondly, the parameters describing the crystallization are also fundamental in the thermal problem and for the adequate coupling between the temperature and the relative crystallinity fields. The numerical simulation of the crystallization is mainly dependent on the Nakamura function $K_{Nak}(T)$ and the crystallization enthalpy ΔH. An error of 3% is added to these variables and the relative errors of

the estimated results are shown in Figure 13. The relative error in the crystallization phase is majorly increased and reaches a value up to 10% with a nonlinear evolutionary profile. Hence, the crystallization parameters have a significant impact on the identification of the thermal conductivity. This observation makes sense since the incertitude of the crystallization evolution will directly influence the thermal response and thus the inverse identification.

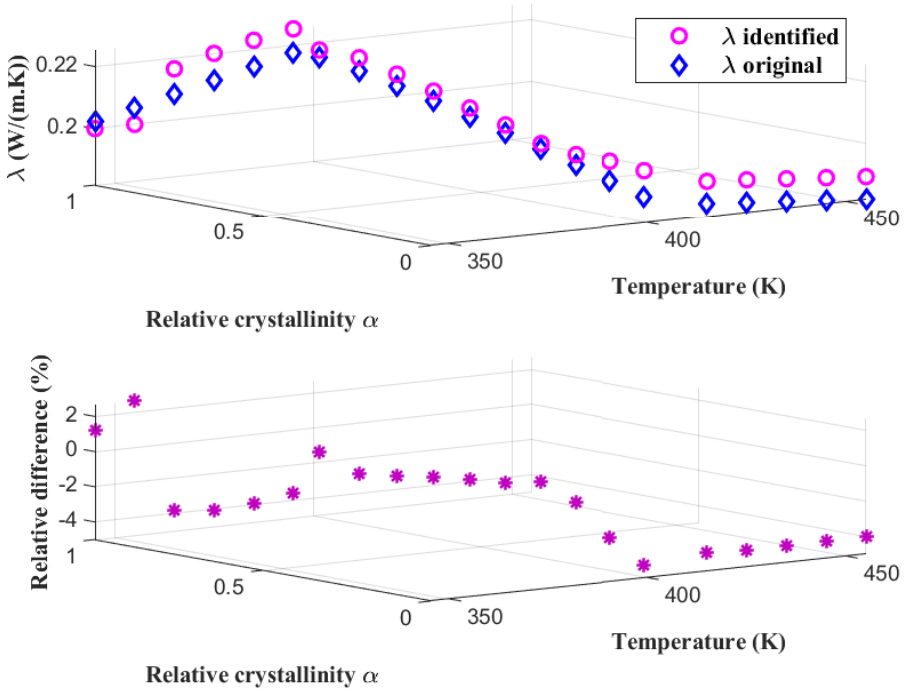


Figure 12: Comparison between the "original" values of the thermal conductivity and the values estimated by the genetic algorithm coupled with the interior point method with an error of 2% on the volumetric heat capacity, with a noise of $0.025°C$

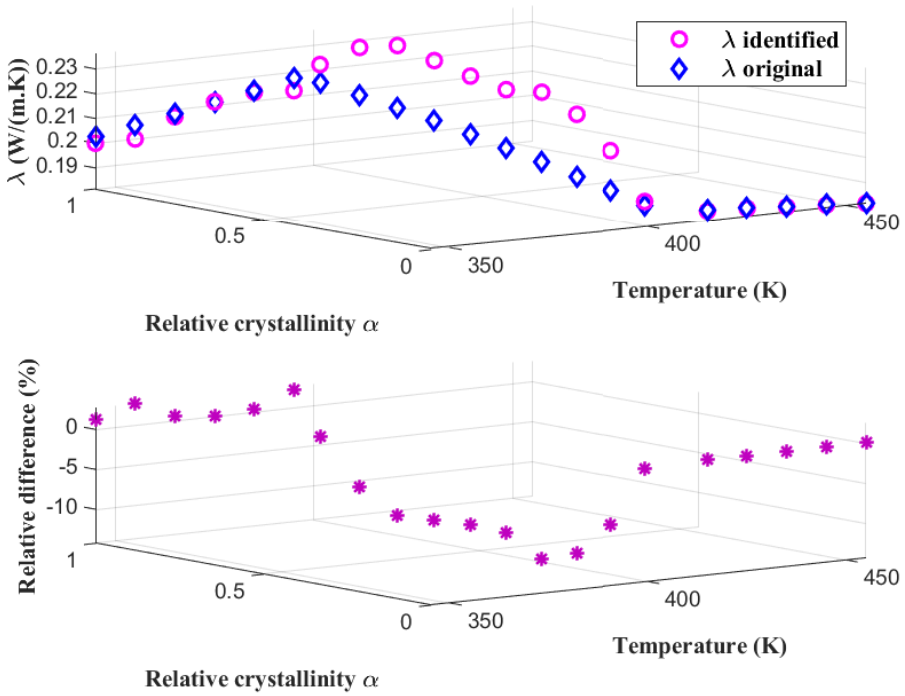


Figure 13: Comparison between the "original" values of the thermal conductivity and the values estimated by the genetic algorithm coupled with the interior point method with an error of 3% on the crystallization parameters, with a noise of 0.025°C

In order to enclose the study of the incertitudes effects, the inverse calculation is repeated while considering the errors on all the parameters previously mentioned in addition to a synthetic noise with a standard deviation of 0.025 °C. On one hand, the inverse problem is solved while adding positive uncertainty percentages to all the parameters. On the other hand, the uncertainties were accounted to be negative. The identified thermal conductivities values of the three phases (liquid, crystallization and solid) are plotted function of temperature and relative crystallinity in Figure 14. These values are compared with the original thermal conductivities as well as the results obtained by the identification without synthetic noise and uncertainties (Section 4.1). It is noticed that the thermal conductivities increase as the values of the density and the specific heat are augmented and vice versa. In this manner, a delimitation is made for the margin within which the estimated thermal conductivities fluctuate depending on potential errors and noise. The minimum and maximum absolute relative errors of the thermal conductivity in the three phases are presented in Table 3. The obtained percentages assist in approximating the marge of error, the results of the identification technique fall within.

This investigation contributes in determining the accuracy level of the results and the aptitude of the identification technique when being applied with real experimental measurements. Indeed, the presence of uncertainties is unavoidable in thermal characterization and may mislead the resolution of the inverse problem. Therefore, it is safe to state that the developed method identifies the thermal conductivity values with an uncertainty of about 20% even though the real evolutionary profile may not be recovered.

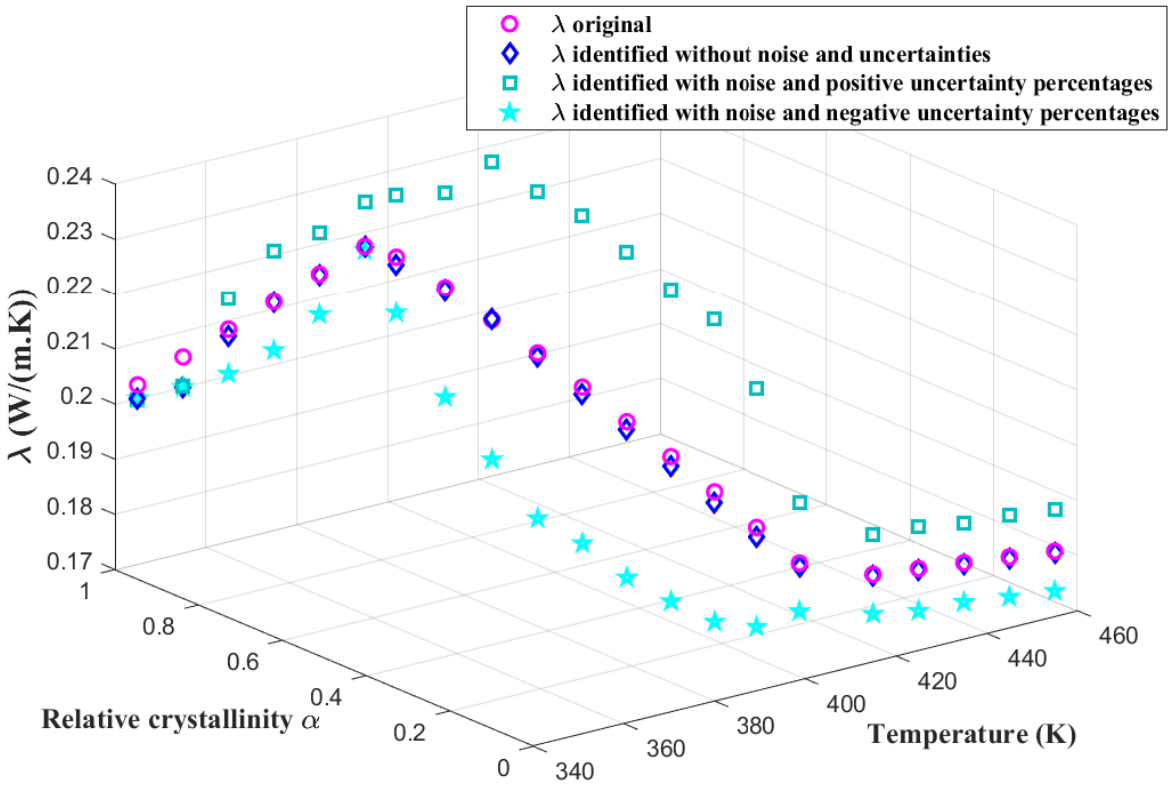


Figure 14: Comparison between the "original" values of the thermal conductivity and the values estimated by the hybrid optimization algorithm function of temperature and relative crystallinity, with and without synthetic noise and uncertainties

Table 3: Minimum and maximum absolute relative errors of the thermal conductivity in the three phases when considering all the possible incertitudes

Phase	Minimum	Maximum
Liquid	0.33%	5.69%
Crystallization	7.85%	24.75%
Solid	1.35%	9.1%

4.3. Identifiable thermal conductivities according to the cooling rate

As previously mentioned in section 3.1, a restricted zone of the thermal conductivity matrix is identifiable based on the crystallization temperature range. This zone is mainly dependent on the cooling rate imposed on the upper and lower surfaces of the polymer. It is reminded that the temperature profiles $T_1(t)$ and $T_2(t)$ are measured with the help of an instrumented mold equipped with a cooling system with several rates. Thus, this section is dedicated to investigate the possibility of changing the matrix's identifiable zone when applying various cooling rates. In case the cooling rate is increased to a value of 20.8 K/min, the crystallization takes place at temperatures ranging between 394 and 404 K. The temperature sensitivities with respect to the thermal conductivities corresponding to this temperature range are computed. The temperature and the relative crystallinity combinations of the identifiable thermal conductivities, highlighted in Table 4, are different from the ones perceptible for a cooling rate of 15.2 K/min (Table 1). The relative errors of the identified thermal conductivity values are also presented. Hence, it is concluded that each cooling rate permits the identification of a different set of parameters with a different accuracy. On another note, the cooling rate

depends also on the position within the thickness of the polymer. Changing the position of the thermocouple will certainly lead to a different cooling rate according to the temperature gradient within the polymer. The identifiable thermal conductivities and their estimation errors are therefore related to the position of the thermocouple, the imposed cooling rate and the thickness of the considered polymer.

Table 4: Relative errors (%) of the identifiable thermal conductivities for a cooling rate of 20.8 K/min

α / T (K)	392	394	396	398	400	402	404
0					15.73	13.46	30.22
0.2					10.11	61	
0.4					17.84	24.15	
0.6				14.29	19.79		
0.8			23.81	14.48	32.12		
1	7.12	29.36	44.6	4.46			

5. Conclusion

This work focuses on the development of an inverse method devoted to the characterization of the thermal conductivity of polymers during their crystallization. The identification process consists in identifying the thermal conductivity evolution function of two coupled fields which are the temperature and the relative crystallinity. An unidirectional heat transfer model is developed to simulate the thermal response of the polymer during its crystallization. The accuracy of the numerical model is priorly validated to be reliably used for the inverse method. A hybrid optimization algorithm combining the genetic algorithm with the interior point algorithm has been shown to be efficient in estimating the thermal conductivity values. The minimization procedure relying on a deterministic algorithm to converge towards the local minimum in the global minimum region identified by the stochastic method, has shown to be crucial for the accurate resolution of the problem. In order to perceive the accuracy of the inverse method, synthetic noisy data is implemented and precise thermal conductivity values are obtained.

The effect of the known thermal parameters uncertainties is also treated in this study. The uncertainty on the volumetric heat capacity does not decrease majorly the precision of the results and thermal conductivity evolutionary profile is preserved. However, in case of an uncertainty of 3% on the crystallization parameters, the relative error of the identified thermal conductivities may reach 20% and the evolutionary profile is distorted. The sensitivity study manifested the possibility of identifying a different thermal conductivity set when changing the imposed cooling rate.

This work has therefore contributed in introducing a new identification strategy that handles the phase change of the material. The originality of this estimation technique is that no predefined evolutionary profile is imposed to solve the inverse heat conduction problem. In this manner, this method allows for the bypassing and validation of currently used variation models.

This analysis is ought to be extended in future works to assess the use of the identification method with experimental measurements. An experimental bench aiming to measure the temperature evolution within a polymer during its crystallization is under execution. The exactitude of the experimentally identified thermal conductivities will be interpreted in the light of the different aspects studied in this work.

Nomenclature

α Relative crystallinity

Δt Time length s

Δx Mesh length m

λ Thermal conductivity $W/(m.K)$

ρ Density kg/m^3

σ	Standard deviation
ξ	Eigen value
a	Thermal diffusivity m^2/s
C_p	Specific heat $J/(kg.K)$
e	Thickness m
GA	Genetic algorithm
K_{Nak}	Nakamura coefficients s^{-n}
n	Avrami index
PSO	Particle swarm optimization
PVT	Pressure Volume T
T	Temperature K ($0\ K = -273.15\ °C$)

Declaration of competing interest

There is no conflict of interest about this submission

Data availability

Data will be made available on request

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