Identification of the thermal conductivity of polymer materials during their crystallization

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Abstract. Controlling the quality of industrial products requires an accurate comprehension of the material’s behavior during the several transformation phases. An accurate estimation of the heat transfers taking place throughout the production phases necessitates the exact knowledge of the thermophysical properties. These properties are well known in the solid state, however they are less mastered in the liquid state and during transformation. The main objective of this research project is to estimate the evolution of the thermal conductivity during transformation by solving an inverse heat conduction problem. The calculation outputs ought to describe the evolution of the thermal conductivity function of two coupled fields: the temperature and the transformation degree. The inverse method relies on a finite difference numerical model and a hybrid optimization algorithm, combining a stochastic method with a deterministic method. The temperature evolution within a thermoplastic undergoing transformation is measured with the help of an instrumented mold. The thermal conductivity values are identified by minimizing the discrepancy between the experimentally measured temperature profile and the one numerically simulated. The acquired results are compared with the mixing law, classically used to take into account the phase change of a material. It is observed that the values acquired by the established inverse method reproduce the measured temperature profiles more accurately than the mixing law.

Introduction
Polymeric materials are widely used in the production industry and the sheer number of their utilizations is as vast as they are diverse. Their versatility and their extensive characteristics range make them the essence of a broad number of productions. The main polymer processing operations are extrusion and injection molding, during which thermoplastics undergo several phase changes [1]. The control of the quality product relies chiefly on the accurate estimations of the heat transfer taking place during the transformation phases. Indeed, a correct prediction of the material's thermal behavior avoids the generation of defects within the manufactured products such as shrink voids, delamination, frozen in stresses [2]. A precise simulation of the heat transfers requires the exact knowledge of the material's transformation kinetics as well as its thermophysical properties which are the thermal conductivity, specific heat and density. As a matter of fact, these properties are very well measured in the solid phase, yet their measurements in the liquid phase and during transformations, are less mastered.

In this context, the thermal characterization of polymeric materials has essentially focused on determining the temperature dependence of the thermophysical properties. The measurement or the identification techniques have only been restricted to a material in its fixed state and not during its transition from a state to another [3]. Until nowadays, no study has addressed the complex evolution of the thermophysical properties function of two coupled fields which are the temperature and the transformation degree. Indeed, inverse heat conduction problems have served...
in estimating the unknown thermophysical properties of different types of materials. The resolution of the inverse problem is achieved by minimizing the discrepancy between experimental measurements and synthetic signals generated by a numerical or an analytical model. In this manner, the thermophysical properties of anisotropic materials were estimated by solving inverse heat conduction problems [4], [5], [6], [7]. Some studies ought to identify the linear evolution of the properties by solving a steady state problem [8], [9] while others investigated the temperature dependence on the thermal conductivity in a transient state [10], [11]. As a matter of fact, the thermal conductivity of a thermoplastic was identified in the liquid and solid state during cooling without taking into account the crystallization.

Furthermore, some authors relied on the traditional mixing law to model the thermophysical properties evolution function of temperature and relative crystallinity [12]. It is theoretically correct to model the heat capacity and the density by the mixing law however it is inconsistent for the thermal conductivity since it is not an extensive property.

Therefore, the main focus of this study is to establish an inverse method dedicated for the estimation of the thermal conductivity evolution function of temperature and relative crystallinity, without imposing an evolutionary profile. For this manner, a numerical model is developed to simulate the thermal response of a polymer during its transformation. A hybrid optimization algorithm combining a stochastic method with a deterministic one is adopted to solve the inverse heat conduction problem. The experimental temperature measurement is achieved with the help of an instrumented mold mounted on a pneumatic press equipped with a cooling and a heating system. The inverse method is applied on a polypropylene sample, whose crystallization kinetic as well as the temperature dependence of its specific heat capacity and density are characterized. The thermal conductivity values obtained for several combinations of temperature and relative crystallinity are compared with the mixing law in order to assess its reliability.

**Inverse method**

**Numerical model.** The developed inverse method consists in estimating the unknown parameters that minimize the difference between the measured temperature profile and the profile numerically computed. For this manner, the thermal response of the polymer, during its transformation, is simulated using a finite difference model. The one directional heat transfer problem is discretized using the Crank-Nicholson scheme. The one dimensional heat equation modelling the thermal response of the polymer is coupled with the exothermal heat generated during the crystallization phase. The heat conduction problem is described by Eq. (1) and (2):

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

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

With \( \Delta H \) being the crystallization enthalpy, \( K_{Nak}(T) \) the Nakamura coefficient function of temperature and \( n \) the exponent of Avrami. The traditional differential form of Nakamura [13,14] was implemented and numerically solved using a simplified equation. Levy [13] proved the robustness and the accuracy of writing the crystallization kinetic in the following form:

\[ \frac{\partial \alpha}{\partial t} = K_{Nak}(T).G(\alpha). \]

With \( G(\alpha) \) a function computed over the interval \([0,1]\).
The boundary conditions considering the imposed cooling rate at the upper and lower surfaces written as:

\[ T(x = 0, t) = T_1(t) \quad \forall \ t > 0. \quad (4) \]

\[ T(x = e, t) = T_2(t) \quad \forall \ t > 0. \quad (5) \]

The initial conditions of the thermal problem are:

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

\[ \alpha(x, t = 0) = 0 \quad \forall \ x \in [0; e]. \quad (7) \]

**Unknowns of the problem.** The resolution of the inverse heat conduction problem ought to identify the thermal conductivity function of two coupled fields which are the temperature and the relative crystallinity. For this manner, the thermal conductivity values, corresponding to the possible combinations of temperature and relative crystallinity, are stocked in a matrix of the following form:

\[
\begin{pmatrix}
T_1 & T_2 & \cdots & \cdots & \cdots & T_{n-1} & T_n \\
\alpha_1 & \lambda_{11} & \lambda_{12} & \cdots & \cdots & \cdots & \lambda_{1n} \\
\alpha_2 & \lambda_{21} & \lambda_{22} & \cdots & \cdots & \cdots & \lambda_{2n} \\
\vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\
\vdots & \vdots & \vdots & \cdots & \ddots & \ddots & \vdots \\
\vdots & \vdots & \vdots & \cdots & \cdots & \ddots & \vdots \\
\vdots & \vdots & \vdots & \cdots & \cdots & \cdots & \vdots \\
\alpha_{m-1} & \lambda_{m1} & \lambda_{m2} & \cdots & \cdots & \cdots & \lambda_{mn-1} \\
\alpha_m & \lambda_{m1} & \lambda_{m2} & \cdots & \cdots & \cdots & \lambda_{mm}
\end{pmatrix}
\]

\[ (8) \]

The matrix is defined by \( m \) levels of temperature and \( n \) levels of relative crystallinity and will assist in computing the thermal conductivity of the polymer during its crystallization. At each time step and at each position of the thickness, the thermal conductivity is calculated by performing a double linear interpolation function of temperature and relative crystallinity. On the other hand, the polymer in the molten and solid states has a fixed relative crystallinity: \( \alpha = 0 \) and \( \alpha = 1 \) respectively. Therefore, the thermal conductivity of the molten and solid polymer is only dependent on the temperature. The thermal conductivity values are, therefore, calculated by a linear interpolation function of temperature.

One should note that the thermal problem may be over-parameterized since the thermal conductivity matrix can not be entirely estimated, based on a single cooling rate experiment. Indeed, the relative crystallinities \( \alpha \), ranging between 0 and 1, are associated with temperature levels according to the crystallization kinetic [14] [15]. The thermal conductivities that can be accurately identified are the ones that are involved in the polymer's thermal response calculations.

**Cost function.** As previously mentioned, the resolution of the inverse heat conduction problem relies on the minimization of an objective function representing the discrepancy between the
experimental temperature measurements and the numerical results. The cost function is described by the following formula:

\[
J = \frac{1}{n \times t_f} \sum_{i=1}^{n} \int_{0}^{t_f} \left( T_{i,Experimental}(\lambda) - T_{i,Numerical}(\lambda) \right)^2 dt.
\]

With \( n \) being the number of points where the temperature variation is measured and computed, \( t_f \) the experiment time length and \( \lambda \) the set of thermal conductivities to identify.

**Optimization algorithm.** The optimization algorithm keeps on adjusting the unknown set of parameters until the cost function satisfies a predefined criterion. The identification of the thermal conductivity values is achieved by combining a stochastic algorithm with deterministic one. The genetic algorithm, mainly inspired from Darwin's evolution theory [16], is capable of handling the great number of unknowns of the complex and non-linear problem. It will contribute in converging towards the region of the global optimum and its stochastic aspect avoids getting trapped in local minima. The values found by the genetic algorithm are implemented as initial value to the interior point algorithm [17]. This deterministic method applies the Newton method on the Lagrangian of the problem while it switches to the gradient conjugate method when the problem is non-convex. The robustness, feasibility and accuracy of the estimation method has been verified using signals, generated by the numerical model and corrupted by a synthetic noise. Based on the experimental measurements registered by a K type thermocouple, a random Gaussian distribution with a standard deviation of 0.025 °C is representative of the measurement noise. In a previous study, the hybrid optimization algorithm was tested and proved to be adequate for the resolution of the inverse heat conduction problem [18]. Furthermore, the robustness of the established inverse method has been evaluated by taking into account the uncertainties on apriori known thermal parameters [19].

**Experimental measurements**

**Material.** The material considered in the present study is an impact polypropylene copolymer, Sabic PP 48M10. According to the supplier, this polymer is characterized by its advanced rheological properties, its high rigidity and its elevated resistance to impacts. It is mainly used in the manufacturing of products having complex shapes, tough packages as well as automobile and electronic components. An experimental campaign aiming to characterize the thermophysical properties of the polymer and its crystallization kinetic is achieved. Indeed, the accurate knowledge of these properties is crucial for an exact identification of the thermal conductivities.

The specific heat \( C_p \) is determined by differential scanning calorimetry by heating a polypropylene sample from 20 °C to 230 °C at a heating rate of 5 K/min. \( C_p \) is then evaluated as a linear function of temperature for both the solid and the amorphous phases. The specific volume \( \nu \) is measured with the help of a home-made PVT device [20] at different pressures of 25, 40 and 50 MPa and at a cooling rate of 2 K/min. Tait model is then utilized to estimate the temperature dependence of the specific volume at atmospheric pressure (or any desired pressure) [21]. The measured data are fitted following a linear regression of temperature for the solid and the amorphous states.

The crystallization of a thermoplastic consists in the formation of a nuclei in the melt and its growth into semi crystalline structures called spherulites. The progress of the crystallization process is perceived through the relative crystallinity \( \alpha \), ranging between 0 and 1. During the molding operation, the crystallization occurs when cooling from the melt state to the ambient temperature. Therefore, the transformation taking place is strongly anisothermal and is best
depicted by the Nakamura model [14], [15]. The differential form of the crystallization kinetic (Eq. 2), developed by Patel et al. [22], requires the Avrami exponent $n$ and the Nakamura coefficient $K_{Nak}$. It is reminded that the Avrami kinetic function, dedicated for modeling isothermal crystallization [23], [24], is linked to the Nakamura kinetic function by $K_{Nak} = K_{Nak} \frac{1}{n}$. In this manner, the crystallization kinetic is investigated through the heat fluxes recorded during the isothermal plateau at temperatures ranging between 135 and 145 °C. In order to study isothermal crystallization at lower temperature values, differential nanocalorimetry is used. As a matter of fact, the DSC Flash allows to quench the polymer at a cooling rate that can reach 10000 K/s. The material is then completely amorphous at the beginning of the crystallization plateau since its anisothermal crystallization has been completely hindered by the high cooling rate. The isothermal crystallization is, therefore, inspected at temperatures ranging between 70 and 118 °C.

Description of the instrumented mold. The identification method is based on experimental measurements reflecting the thermal behavior of a polymer during its transformation. Therefore, an experimental bench has been developed for this purpose and is composed of an instrumented mold mounted on a pneumatic press. The mold, represented in Fig. 1, is composed of two main parts: the fixed part, with the molding cavity, and the mobile part. The molding cavity has a square shape with a length of 70 mm and allows the stretching of three thermocouples at distinct positions of the thickness, as shown in Fig. 2. The thermocouples have a diameter of 80 μm and are fully embedded in the molded material undergoing cooling and heating cycles. The mobile part allows the cooling of the material by circulating water or air on the top of the molding cavity. The piece, of thickness 5 to 6 mm, is molded under a constant pressure. The mold is placed between the two plates of a pneumatic press (Fig. 2), exerting pressure on the material, and equipped with a cooling and a heating system.

In order to reproduce accurate industrial conditions, the overall heating system is designed to reach a temperature of 400 °C. An additional cooling cycle can be applied on the molded piece by circulating water at 15 °C or air within the plates of the press. The purpose of this design is to apply asymmetric cooling at different rates which allows the crystallization occurrence at different temperature ranges. In fact, varying the cooling rate is convenient to inspect the thermal conductivity values corresponding to a broader crystallization domain.

Experimental protocol and measurements. Prior to placing the polypropylene granulates in the molding cavity, the thermocouples are stretched and the mold is mounted on the press. A mass of 25 g is required to achieve a thickness between 5 and 6 mm. The granulates are firstly melted at atmospheric pressure and at a temperature of 190 °C. After the complete fusion of the material, the mold is closed and the temperature acquisition is started. A constant pressure of 0.8 MPa is applied to maintain the contact between the upper part of the mold and the polymer during the heating and the cooling cycles. The thermocouple responses are recorded using a multichannel acquisition system. This system allows obtaining on the same support the measurement registered by all the thermocouples at an acquisition frequency of 10 Hz.
The precision of the overall system acquisition and experimental bench has to be verified. For this purpose, the repeatability and the reproducibility of the measurements are evaluated. The repeatability has been examined by repeating the measurements on the same molded piece using the exact instruments and without modifying any experimental condition. On the other hand, the reproducibility is tested by applying the same experimental protocols on different molded pieces of polypropylene. The obtained measurements have then been compared and the recorded temperature profiles are repeatable and reproducible (not shown here for reasons of space). This study emphasizes the fidelity and the reliability of the measurements that reflects the thermal behavior of the polymer during its transformation.

Furthermore, the first step in the mold development was to ensure a unidirectional heat transfer through the thickness of the polymer. For this manner, two configurations of the mold have been compared with the help of the commercial finite element software Comsol Multiphysics. The three dimensional configurations are identical and differ only in the boundary conditions. The first model is unidirectional as a Dirichlet boundary condition is imposed to its upper and lower surfaces while its lateral surfaces are considered to be adiabatic. The second model is three directional since a Dirichlet boundary condition is applied on all its surfaces. The temperature profiles at different points of the thickness are simulated and a comparison is done between the outputs of both models.
The maximum temperature difference was found to be 3.5 \( K \) at the corners and does not exceed 0.03 \( K \) along the axis of the component where the thermocouples are positioned. As a result, the heat transfer is regarded as unidirectional as considered in the direct model.

Once the measurements are terminated, the molded piece is retrieved from the mold and cut perpendicularly to the thermocouples direction. The positions of the thermocouples are then localized by optical microscopy.

**Results and discussion**

The overall temperature measurements as well as the characterized thermophysical properties and the crystallization kinetic are implemented in the inverse method to estimate the unknown parameters. The melted polymer is cooled by circulating water within the plates of the press. The mobile part of the mold is not subjected to a cooling cycle in order to accomplish crystallization at a slow cooling rate. The temperature evolutions measured by the upper and lower thermocouple are considered to be the boundary conditions while the middle thermocouple is used for the cost function computation. The outputs of the inverse calculations depict the thermal conductivity evolution in the solid state, amorphous state and during crystallization as represented in Fig.3. In order to evaluate the values estimated in the liquid and solid states, the obtained results are compared with thermal conductivities issued from the laser flash analysis [25]. It is reminded that this non-intrusive characterization method assists in determining the thermal diffusivity \( \alpha \) that is linked to the other thermophysical properties by the following relation: \( \alpha = \frac{\lambda}{\rho C_p} \). The identified thermal conductivities of the amorphous polymer are in good agreements with the ones obtained by the laser flash analysis. However, the thermal conductivities of the solid state are overestimated due to the low temperature gradient, indicating the low sensitivity of the temperature to the unknown parameters. It is noted that the average temperature gradient is around 2 \( K/mm \) in the solid state, whereas it reaches 6 \( K/mm \) in the amorphous state.

The variation obtained during crystallization is compared with the classical mixing law. It is observed that the identified thermal conductivity does not follow a linear variation function of temperature and relative crystallinity. The assessment of these results is achieved by computing the temperature residuals corresponding to three possible cases as depicted in Fig. 4. The thermal conductivities identified by the inverse method reproduce with high precision the recorded temperature evolution since the temperature residual is well-centered and have a standard deviation of \( \sigma = 0.05 \deg C \). It is noted that the standard deviation of the experimental temperature noise is \( \sigma_{\text{Noise}} = 0.025 \deg C \). The thermal conductivities used in the second and the third cases are computed by applying the mixing law based on the values identified in the solid and amorphous states and the values measured by laser flash analysis, respectively. The temperature profiles generated are not as adequate as the first case considering the temperature residuals that have drastically increased. The purpose behind using the same law with different values is to evaluate its reliability without being constrained by the potential inexact estimation of the inverse method. As observed, the results of the solid state are misleading. Nevertheless, it is concluded that the mixing law is not representative of the actual thermal conductivity evolution during the polymer crystallization. This conclusion emphasizes the fact that the thermal conductivity is not an extensive property and is not linearly dependent of the transformation degree.
Fig. 3 Comparison between the identified thermal conductivity values, the values computed from the mixing law and the values found by laser flash analysis.

Fig. 4 Comparison of the measured temperature profile with each of the temperatures profiles computed using the identified thermal conductivities, the mixing law based on the values identified in the solid and amorphous states and the mixing law based on the values measured by laser flash analysis.
Summary
An estimation of the thermal conductivity evolution during the polymer crystallization is presented in this paper. The unknown parameters are identified by minimizing the discrepancy between the temperature evolution experimentally measured and the profile numerically computed. The inverse heat conduction problem is solved by adopting a hybrid optimization algorithm combining the genetic algorithm with the interior-point method. The temperature evolutions within a polymer undergoing crystallization are recorded with the help of an instrumented mold. The mold is mounted on a pneumatic press equipped with a cooling and a heating system allowing the fusion of the polymer and its crystallization at different cooling rates. Prior to applying the inverse method, an experimental campaign is achieved in order to characterize the crystallization kinetic of the studied polymer as well as the temperature dependence of its specific heat and density. The results obtained by the inverse calculations represent the thermal conductivity evolution in the solid state, liquid state and during crystallization. The values found in the amorphous and solid phases are compared with the values experimentally measured by laser flash analysis. The thermal conductivity of the amorphous polymer is accurately estimated contrary to the thermal conductivity of the solid polymer. The evolutionary profile estimated function of temperature and relative crystallinity is compared with the classical mixing law. It is observed that the estimated thermal conductivities do not obey a linear rule and reproduces the measured temperature with a greater accuracy than the mixing law. The next step will consist in applying the inverse method with several cooling rates in order to cover a broader crystallization domain. In fact, varying the cooling rate contributes in identifying the thermal conductivities corresponding to a multitude of temperature and relative crystallinity combinations.

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