Heat Transfer in Polymer Composite Materials

Forming Processes

Edited by
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This book is a recapitulation of the CNRS Summer School organized in June 2013 dedicated to heat transfer in organic matrix composite materials and their forming processes. The industry of composites has grown steadily in recent years due to the numerous advantages of these materials, such as their lightness and interesting mechanical properties, compared to aluminum and other metal-based alloys. To remain competitive, especially in a very strong international economic context, the quality of the produced parts must be fully controlled. This control requires an accurate knowledge of physical phenomena occurring during the various steps of their manufacturing process and in a context where the strong activity and the needs led to the emergence of new processes and increasingly fast production rates. The forming of composite materials has thus become a major topic of research in terms of experimentation, modeling and simulation, where several scientific disciplines must come together in order to achieve the control of manufactured parts and properties. We can notice that heat transfer is one of the main levers to control the forming processes and induced properties of the composite part. They have to be carefully analyzed during the manufacturing of these materials that also require a multidisciplinary approach. Thus, thermal sciences have to be coupled to other scientific fields such as mechanics and physical chemistry.

The first goal of this summer school was to bring together academic and industrial researchers from different disciplines within thermal sciences with transverse themes common to their activities. A second aim was also to provide the basis on heat transfer during polymer and composite processing as well as the latest methods and techniques from experimental, numerical and modeling points of view, useful to help in the solving of many issues. Therefore, the book takes this and gives theoretical and practical information to understand, measure and describe, in a relevant way, heat transfer during forming processes (in the tool as well as in the composite part) and introducing the required couplings. For this purpose, we relied on the experience of recognized French researchers.
This book is written in a comprehensive way for an audience that is already aware of the world of composites and associated processes: graduate students, researchers and people involved in R&D activities in industrial sectors. Our aim is to provide a tool, useful for the readers to start a study on composite processing where heat transfers are involved. Each chapter describes the concepts, techniques and/or models related to the developed topic and several examples are given for illustration purposes. A list of selected references is also given at the end of each chapter for a deeper complement of its content, which is necessary for more complex analyses and developments. Unfortunately, all topics and issues related to heat transfer in composite parts and processes cannot be addressed in a single book and a selection was made to cover a broad range of subjects and associated issues.

The introductive chapter presents heat transfer analyses and issues in polymer and composite processing through illustrative examples mostly from injection molding. Preconceived ideas, difficulties and simplified approaches are well highlighted. One key to success in heat transfer modeling is the accurate knowledge of thermophysical properties, phase change kinetics and their associated models for both thermosets and thermoplastics. Conventional as well as new methods to experimentally determine these properties and reaction rate parameters as a function of temperature are detailed in Chapters 2 and 3. Scientific and technical issues are also included. A comprehensive review of the effects of thermoplastics process conditions (shear and/or elongation induced by the flow) and the addition of other components (nucleating agents, fibers, etc.) on the transformation kinetics of the polymers, their rheological behaviors and final microstructures is detailed.

From all these data, the simulation of residual stresses developed during the matrix transformation and the cooling is discussed. For this purpose, thermokinetic and mechanical couplings are introduced and the prediction of cure-dependent mechanical properties is presented. In Chapter 6, modeling of heat transfer in multi-scale porous media, which can be encountered during the filling step of Resin Transfer Molding (RTM) mold, is discussed following a homogenization approach. The relationship between the physics at local-scale and the macroscale description is explained, also including the determination of effective properties.

The improvement of the quality of parts can be achieved by optimizing process parameters. Among them, the thermal control of the part is of strong importance and depends on the thermal control of the mold. Thus, optimization approach has to consider heat transfer in the tool and couplings to include contact conditions and transformation kinetics. Context, definition and methods of optimization are covered in this book and are illustrated with two detailed examples. Process modeling is introduced in Chapters 8 and 9. First, we discuss the peculiar case of thermoplastic welding, where no adding material is required for assembling. The importance of intimate contact and macromolecular diffusion is emphasized from theoretical and
practical points of view, including the strong temperature dependence. A simulation of forming processes is also addressed in a more general way. Several examples are proposed to present multiscale, multiphysics and multidomain modeling, which are representative of the complexity of forming processes.

Another important part in heat transfer analysis concerns the instrumentation for the thermal characterization and the control of manufacturing processes. From these data, it is possible to obtain information about the process, thermophysical properties and/or the matrix transformation (for example, using inverse method algorithms). An overview of the existing instrumentation (contact and contactless methods) is given in this book. A specific chapter has been specifically dedicated to heat flux sensors, since they provide relevant information to quantify heat transfer between the part and the tool. It is thus an important complement to temperature measurement. Available heat flux sensor technologies and their main characteristics are also mentioned and are completed with practical examples.

Toward the final part of this book, radiative heat transfer in polymer and composite forming are detailed. The processes using infrared heating are in development and the complexity of heat transfer analysis leads to several scientific issues. After a presentation of the basics to define thermal radiative properties, measurements are presented for classical semi-crystalline polymers and associated composites. Finally, after a description of infrared emitters and the temperature measurement using infrared camera, modeling of radiative heat transfer is introduced and polymer processing applications are included.

I would like to thank all my French colleagues who have done me the honor of participating to the CNRS Summer School in 2013 and then of accepting to contribute to this book project with their high-quality work. Special recognition goes to Didier Delaunay, CNRS senior researcher, for his scientific involvement and significant contribution to research in heat transfer in composites and forming processes. I hope that all readers, working in the broad field of polymer and composite processing, may find this book an interesting and valuable resource.

Nicolas BOYARD
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Introduction to Heat Transfer During the Forming of Organic Matrix Composites

In this chapter, we present some very illustrative examples of advances obtained in the analysis of the heat transfer in the forming processes of composites. These examples highlight at the same time the difficulties and scientific issues, as well as some simplified approaches to obtain, in an accessible way, a rapid estimation of the times of cooling or heating of a composite part. We also point out some preconceived ideas, in particular on the nature of transfers during the filling of molds in injection process, and for this we propose a new criterion to determine the transition between the thermal shock regime and the one of established convection, which is validated by experimental results. The selected processes are the injection of composites with short fibers (thermoplastic and thermosets), and the injection on a fabric. The examples are illustrated by results issued of more than 25 years of analysis of heat transfer in the processes, during thesis led within the framework of partnership programs with companies of the plastics processing industry. Finally, some directions for new developments are proposed.

1.1. Introduction

The mastery of composite forming processes raises a number of challenges on heat transfer and how to take them into account adequately. Indeed, the nature of these materials itself induces peculiarities. First, they have at least two components, which poses the problem of determining their effective properties according to those constituents. Composites are also multi-scale materials: the fibers are gathered into tows, which are woven to make a fabric. Reinforcements, but sometimes also the matrices, are anisotropic. The coupled phenomena introduce complex physics difficult to interpret without thorough knowledge of them and their interactions. Furthermore, the operating conditions in the process can be often considered as extreme. High cooling rates are frequently encountered, such as for the contact
between a cold mold and a hot composite. Shear rates can be very large at the wall of
an injection mold, or in the micro channels between fibers (even if the flow rates are
low). To compensate the shrinkages due to the cooling or the transformations,
pressures are sometimes very high in the molding cavity (up to 200 MPa for injection).
Low-conductive polymers and composites are in some cases subjected to overheating
as a result of heat source release induced by transformation. An additional issue is the
fact that the temperature measurement is very difficult because it is intrusive. It is not
yet well known how to experimentally determine the temperature fields within a
molded part or inside of the plies in a reinforcement stack. The size of thermocouples,
which should be at least as small as the fibers, makes them very fragile, especially in a
viscous fluid flow. To date, the precise determination of the inlet temperature in the
injection channel of a mold is an open problem. Another particularly characteristic
example is the location of the filling fronts and the saturation distribution in a
composite made by liquid composite molding (LCM) since it is coupled to heat
transfer. In addition, solving a heat transfer problem requires the accurate knowledge
of the boundary conditions, which may be difficult. We can also give the example of
the determination of the thermal contact resistance (TCR) to the wall of a molding
cavity or between plies during the consolidation of a composite.

Temperatures are important to know, but the dynamics of a thermal system may
be assessed only by measuring the heat flux. How to make a heat flux sensor non-
intrusive and accurate in the environment of forming processes? The main question
is ultimately whether a fine thermal knowledge is essential to achieve quality parts.

In this chapter, we will show, from a few illustrative examples, that the
couplings involved at all levels must be adequately taken into account from the point
of view of heat transfer, since they induce consequences on the quality of the final
product appearance, size, shape and properties. The thermal scientific problem
appears as inevitable, especially since productivity requires short cycles in mass
production: there is indeed cycles of about 1 min for automotive parts. Everyone can
easily understand that the heating and cooling of a part by varying its temperature
sometimes several hundred degrees in very short times, with the objective to control
the temperature fields and to obtain uniform final properties for complex shapes,
requires a non-trivial strategy.

1.2. Examples of injection of short fiber reinforced composites

1.2.1. Heat transfer during the filling phase

1.2.1.1. Case of semi-crystalline polymer matrices

We will first discuss the injection of a polymer reinforced with glass fibers,
taking the example of a widely distributed poly-aramid, whose trade name is IXEF
The scope of this study is a collaborative program (“FISH” program) involving LTN, IMP (Lyon), PIMM (ENSAM Paris) laboratories and Moldflow, Legrand, and Solvay companies.

An injection cycle is typically divided into four phases: the filling step (few seconds) is short compared to the total cycle time, during which high shear rates may occur. The packing phase consists of applying a pressure on the polymer/composite to compensate the thermal and crystallization shrinkages. The third step is the isochoric cooling under pressure after the gel of the injection gate, preventing the entry or exit of polymer from the molding cavity and finally the cooling at atmospheric pressure after the possible unsticking of the part. At the end of the cooling, the solid polymer part is ejected and the new cycle can begin.

![Figure 1.1. Heat flux to the wall of a molding cavity in injection process](image)

The thermal behavior of the mold is periodic: the heat flux exchanged between the part and the mold is very large at the beginning of the cycle, decreases and finally is negative at the ejection, as shown in Figure 1.1. This particularity has to be taken into account since an established periodic state is required for constant quality parts. The typical example of heat flux at the wall of a molding cavity displayed in Figure 1.1 highlights a dramatic and very quick decrease. How can we interpret this behavior? Let us consider the flow in the channel formed by the molding cavity. If we assume legitimately that the forced convection is in the steady...
state, it is possible under these conditions to evaluate a local Nusselt number at the
distance x from the entry of the molding cavity using a conventional correlation for
a prescribed wall temperature [PIN 09], for a shear thinning fluid with a rheological
power law type:

\[ \text{Nu}(x) = \frac{1.16(3n + 1)/(4n)^{1/3}}{(\text{PeD}_h/x)^{1/3}} \]  

[1.1]

The Peclet number is defined as \( \text{Pe} = \frac{V \text{D}_h}{a} \); \( \text{D}_h \) is the hydraulic diameter of the
channel, here twice its thickness, \( a \) is the diffusivity of melt, \( n \) is the index of the
power law viscosity. For the considered instrumented molding cavity [LEG 06]
(incomplete part is shown in Figure 1.2 and instrumented cavity in Figure 1.10), we
obtain the position of the sensor near the gate a value of 20 for the Nusselt number,
which corresponds to a constant heat flux during the filling phase close to \( 1.10^5 \)
W/m². The heat flux obtained as such (see detailed calculations in section 1.2.1.2
applied for bulk molding compound (BMC) processing) is the good order of
magnitude (see Figure 1.1) but the experimental one decreases very quickly and we
do not observe a constant value even during a short time. The analysis is thus
invalidated: the evolution of the heat flux does not correspond to a regime of
established convective exchange between the polymer and the wall of the molding
cavity. Here is a preconceived idea, which constitutes an approach nevertheless
classic but erroneous.

Let us test then the hypothesis that the heat flux decrease is due to the coupling
with the conduction in the mold. There is an analytical solution [CAR 59] to the
problem of a flowing fluid, which is suddenly put into contact with a wall. In this
solution, exchanges by convection are based on a constant convective heat transfer
coefficient \( h \). This latter, calculated from the equations [1.1] and [1.11], is in this
case approximately equal to 660 W/m²/K (we take the value \( n = 0.308 \)). The heat
flux density is given by

\[ \Phi(t) = h F(t/\tau) (T_m - T_i) \]

\( T_m \) is the average temperature of the
melt, and \( T_i \) is the initial temperature of the mold. \( F \) is a decreasing function of time
[CAR 59]. \( \tau \) is given by \( \tau = \frac{\lambda^2}{h^2 a} \), where \( \lambda \) is the mold thermal conductivity and
\( a \) is the melt diffusivity. For the molding cavity studied, we find \( \tau = 35586 \) s, which
corresponds to about 10 h. The rapid decrease in the observed heat flux is
completely incompatible with this law since for \( t = \tau \) the value of the function \( F \)
is approximately 0.4. The result of this analysis using a reductio ad absurdum that
convective heat transfer during the filling phase is not the key to analyze the heat
transfer with the mold.

Let us consider the incomplete part shown in Figure 1.2. The energy equation for
the filling of the molding cavity may under certain simplifying assumptions
(constant thermophysical properties in particular) be written as:

\[ \rho C_p \frac{\partial T}{\partial t} = \beta \frac{\partial T}{\partial t} + \eta \dot{\gamma}^2 + \lambda \Delta T + Q \]  

[1.2]
In this equation, D/Dt is the operator (∂/∂t + V.grad). The left term represents the thermal inertia. The first term on the right is due to the compressibility. The analysis of its order of magnitude shows that in first approach, it can be neglected. The second term is due to the viscous dissipation. Although it is not always negligible, it is also an order of magnitude lower than the other terms, especially early in the filling phase. The third term is the thermal diffusion, which occurs mainly in the z direction. Q is the possible source due to the phase change of the polymer (in the case of semi-crystalline thermoplastics, for example). A commonly accepted hypothesis is that transfers are one-dimensional (1D) along z, so that we can neglect viscous dissipation and the effect of the compressibility. Equation [1.2] can be thus simplified:

\[ \rho C_p \left( \frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} \right) = \lambda \frac{\partial^2 T}{\partial z^2} \quad [1.3] \]

The second term of the left side equation [1.3] is, at the beginning of the filling phase, of several orders of magnitude, lower than the first one. Indeed, the term \( \frac{\partial T}{\partial t} \) is very large and takes precedence over the other. We can then neglect this one and the equation is reduced to the classical 1D Fourier equation:

\[ \rho C_p \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial z^2} \quad [1.4] \]

The part is then subjected to a heat shock: for a short time (fast filling), it can be assumed that during this stage only the surface layers of the part and the mold in the vicinity of the wall of the molding cavity are involved in heat exchanges. The temperature field is thus the one observed in two semi-infinite media suddenly put
into contact. At this time, the temperature in the polymer can be assumed to be uniform and equal to the injection temperature $T_{\text{inj}}$. The temperature in the vicinity of the molding cavity wall is quasi-uniform and equal to the temperature of the mold surface at the time of the beginning of the filling phase. We denote it by $T_{\text{mi}}$. The solution of the contact problem is well known. In the case of an amorphous polymer, if we neglect the contact resistance between the mold and the polymer, the mold surface temperature $T_c$ at the contact time is given by equation [1.5]

$$T_c = \frac{\left( T_{\text{inj}} b_p + T_{\text{mi}} b_m \right)}{b_p + b_m} \quad [1.5]$$

In this equation, $b_p$ and $b_m$ denote, respectively, the effusivity of the polymer and the mold, given by the square root of the product thermal conductivity $\lambda$, volumic mass $\rho$ and specific heat $C_p$: $b = \left( \lambda \rho C_p \right)^{0.5}$. Let us apply this result on the example presented in Figure 1.3, where the time evolution of the mold surface temperature is plotted for the injection of an ABS in a steel mold. The thermal properties of this steel are $\lambda = 36 \text{ W.m}^{-1}.\text{K}^{-1}$, $\rho = 7850 \text{ kg.m}^{-3}$, $C_p = 460 \text{ J kg}^{-1}.\text{K}^{-1}$.

**Figure 1.3. Surface temperature of a mold during injection of an amorphous polymer (ABS)**

The injection temperature of the molten polymer is $240^\circ\text{C}$. In a periodic regime, we can see that the experimental temperature of the injection mold, which is the
minimum value of the curve, is about 64.7°C. The effusivity of the mold steel is 11,474 J.K\(^{-1}\).m\(^{-2}\).s\(^{-1/2}\). The ABS used for this test had the following properties: thermal conductivity \(\lambda = 0.2\) W.m\(^{-1}\).K\(^{-1}\), density \(\rho = 961\) kg.m\(^{-3}\), specific heat \(C_p = 2,300\) J.kg\(^{-1}\).K\(^{-1}\). Its effusivity is, therefore, 665 J.K\(^{-1}\).m\(^{-2}\).s\(^{-1/2}\). From equation [1.5], the contact temperature is equal to \(T_c = 74.3\)°C. This value is obviously very close to the recorded maximum temperature reached by the molding cavity surface, which corresponds to the time of contact of the mold with the hot polymer. This first result is in line with the validation of the heat shock phenomenon governed by the conduction in the part thickness. We note a temperature range of 10 K for the increase in the wall temperature. This result is classic. Soon after, the temperature decreases, because the condition of semi-infinite medium is only valid in the first times of the cycle for a dimensionless characteristic time \(\tau = at/e^2< 0.05\) (empirical result). In the expression of \(\tau\), \(a\) is the thermal diffusivity of the polymer and \(e\) is the half-thickness of the part. In our case, \(e = 1.5.10^{-3}\) m and the diffusivity of the ABS is \(9.10^{-8}\)m\(^2\).s\(^{-1}\). The corresponding time below which the assumption of infinite medium is valid is 1.25 s. From the end of the filling that lasts 1 s, the core temperature of the part decreases and, as a result, the surface temperature.

The heat flux exchanged between the part and the mold associated with equation [1.5] is decreasing and is given by:

\[
\Phi(t) = \lambda (T_{inj} - T_c)/\sqrt{\pi at} \quad [1.6]
\]

This expression of the heat flux, inversely proportional to the square root of the time, is consistent with the experimental observation. It was compared with the experimental data recorded during the injection of an isotactic polypropylene [LEB 98]. Figure 1.4 illustrates the good description of the experimental heat flux by this law during the filling phase, within the first second after contact, when the polypropylene is in the molten (and thus amorphous) state. Then, the beginning of the crystallization is observed, since it induces an increase in the heat flux. At this time, the model deviates from the experiment since it cannot take into account the effect of the phase change. This result completes the demonstration that in the early time of the injection cycle, conductive thermal shock allows us to interpret perfectly the heat exchanges between the part and the mold. Is it possible to transpose this result to a charged polymer, additionally for a semi-crystalline one?

The first approach is to consider the neat matrix. Figure 1.5 displays a typical example of the wall temperature of the molding cavity for the injection of a semi-crystalline polymer [SOB 13].
Figure 1.4. Comparison between the heat flux given by equation [1.6] (dotted line) and the measurement (solid line) in thermal shock regime during the injection of an isotactic polypropylene [LEB 98]

Figure 1.5. Wall temperature in the molding cavity during the injection of isotactic polypropylene [SOB 13]

Unlike amorphous polymers, we observe that the temperature curve shows a net plateau during the first seconds before the decreasing due to cooling. This is due to
the latent heat of crystallization. The solution of a thermal shock problem with phase change (Stefan problem [SOB 13]) induces a change (in comparison with the classical case) of the contact temperature equation [LOU 97]:

\[ T_c = \frac{b_s T_F + b_m \text{erf}(\xi/v)T_{mi}}{b_s + b_m \text{erf}(\xi/v)} \]  \[ 1.7 \]

In this relation, \( v = \sqrt{a_s/a_l} \) where \( a_s \) and \( a_l \) are the solid and liquid (i.e. molten) phases diffusivity, respectively. \( \xi \) is the solution of the transcendental equation

\[ Ste_s \frac{e^{-\xi^2/v^2}}{\text{erf}(\xi/v)} - Ste_l \frac{e^{-\xi^2}}{\text{erfc}(\xi)} = \sqrt{\pi} \xi; \quad t > 0 \]  \[ 1.8 \]

where \( Ste_i = C_p_i (T_{inj} - T_F)/L, \quad Ste_s = C_p_s (T_F - T_c)/L \) are, respectively, the liquid and solid Stefan numbers. \( T_F \) is defined as the temperature of the crystallization quasi-plateau that appears in the core of the polymer upon cooling [SOB 13]. This is a new thermophysical characteristic, which depends on the pressure conditions. It can be determined experimentally or by simulation taking into account the kinetics of crystallization and its changes under pressure. The iterative solution of equations [1.7] and [1.8] allows calculating \( \xi \) and \( T_c \). The quasi-plateau observed in the core of the part is related to the heat released during the crystallization, maintaining \( T_F \) until the complete solidification. Therefore, the constant half-thickness temperature is imposed, which has the effect to extend the semi-infinite character of the phenomenon, hiding what happens “behind” the isotherm \( T_F \). This plateau, therefore, lasts until complete solidification of the part. What happens if we add short fibers to the semi-crystalline polymer?

Figure 1.6 shows a typical example of the evolution of the mold surface temperature during the injection of a poly-aramide reinforced with short glass fibers. A temperature plateau is clearly observed and its time is even longer than the reinforcement ratio is low. This is related to the solidification time since the latent heat decreases when the reinforcing ratio increases. The plateau temperature is also even higher than the reinforcing ratio increases. It can be explained by the increase in the contact temperature induced by both the increase in \( \xi \), when latent heat decreases (the solidification is faster) and the increase in the effusivity of the composite when the glass fiber weight ratio is higher. The accurate calculation of \( T_c \) confirms these effects and the experimental results. 1D heat transfer in the composite through the thickness of the part has been demonstrated in several studies.
[DEL 11, LEG 10, LEG 11], the fibers being oriented in the part in a core-skin structure.

![Diagram](image)

**Figure 1.6. Molding cavity wall temperature during the injection of poly-aramide composites [LEG 06]: no fiber (IXEF 6002), 30 wt% fiber (IXEF 1002), 50 wt% (IXEF 1022)**

This characteristic behavior has the advantage of applying the method described in [SOB 13] to easily estimate the cooling time of the composite part and thus to choose the optimum molding parameters. Indeed, observing Figure 1.6, we note that the molding cavity surface temperature may be less than 1 K with accuracy schematically described by successively a plateau (ordinate $T_c$) and the negative slope line connecting the point corresponding to the solidification time with ordinate $T_c$ (120.5°C for Ixef 6002) to the point corresponding to the part ejection (39 s, 116.5°C for Ixef 6002). The solidification time may be calculated analytically [SOB 13]. It is then possible to analytically calculate the temperature changes in the part and therefore the time for which an ejection criterion is reached. Needless to say that such a simplified approach is not a substitute for professional software that continuously become more accurate, as Moldflow© for example, but it provides the expert with a relatively precise and very quick estimate. This reduced model is also an advantage for optimization software that uses intensively direct problems for solving.