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A more reliable DSC-based methodology to study crystallization kinetics:
Application to poly(ether ketone ketone) (PEKK) copolymers

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HIGHLIGHTS
• Method is based on derivative expression for crystallization Hillier model.
• Model fitting directly on the crystallization heat flux measured by DSC.
• The method avoids the extrapolation of the crystallization peak beginning.
• PEKK Crystallization kinetic modeling including primary and secondary crystallization.

ABSTRACT
To quantify the isothermal crystallization kinetics of poly(ether ketone ketone) (PEKK), the integration of the crystallization peak measured using differential scanning calorimetry is rendered difficult due to the thermal transient effects at the start of enthalpy recording. The different attempts to extrapolate this peak beginning often lead to false values of the Avrami exponent. A new crystallization kinetic assessment method is established here based on the derivative of the Hillier crystallization kinetic model. This method consists of directly fitting the transformation rate to the heat flow of the experimental crystallization, thus avoiding the extrapolation of the crystallization peak beginning. This method is successfully applied to two different PEKK grades with different crystallization kinetics. The identified crystallization parameters are modelled as a function of the crystallization temperature, and based on these modeling results, time-temperature-transformation diagrams of crystallinity were built to provide a useful tool for PEKK processing.

1. Introduction
High-performance poly(ether ketone ketone) (PEKK) thermoplastics are currently studied with great interest by the aeronautic industry as a matrix for carbon-fibre reinforced structural parts. In fact, PEKK composites can be consolidated out of autoclave, while they have lower processing temperatures than poly(ether ether ketone) (PEEK) composites. The final mechanical performances of composite parts are closely linked to their processing. Depending on the thermal processing cycle, the matrix properties as well as the interaction between the matrix and carbon fibres are modified. During the manufacturing of PEKK composite parts, the composite is first heated above the matrix melting temperature to decrease the viscosity of the matrix in order to evacuate all porosity under pressure. This step is known as consolidation. The composite part is then cooled to room temperature. During this step, the matrix may crystallize with a different crystallinity ratio depending on the cooling conditions that directly impact the final mechanical performances of the composite part [1–6]. For this reason, PEKK crystallization kinetics should be controlled in order to optimize the processing parameters in terms of the mechanical performances and processing times of the composite parts.

The crystallization mechanisms of PEKK copolymers have been studied by different authors [7–10] who have shown that similarly to PEEK, PEKK copolymers crystallize with two different crystallization processes, namely a primary crystallization that appears at the early stage of crystallization and a secondary crystallization corresponding to the enhancement of crystallization with the growth of a crystalline structure within lamellae [7]. This subsidiary crystallization should be
taken into account in the crystallization kinetic model. Among the
different crystallization kinetic models that consider this two-step
crystallization, it was previously argued [10] that Hillier [11] proposed
a good model with secondary crystallization kinetics directly dependant
on the primary crystallized volume. Hsiao et al. [8] proposed an ex-
tension of this model by considering that the Avrami exponent of sec-
dondary crystallization $n_2$ could have values other than 1; the total re-
limited relative crystallinity $a(t)$ thus evolves as:

$$a(t) = w_1a_1(t) + w_2a_2(t)$$

(1)

with the respective primary and secondary crystallization expres-
sions:

$$a_1(t) = 1 - \exp\left(-K_1t^n\right)$$

(2)

$$a_2(t) = K_2n_2\int_0^t \left[ 1 - \exp\left(-K_1\theta^{n_1}\right) \right] (t - \theta)^{n_2-1} \exp\left[-K_2(t - \theta)^{n_2}\right] d\theta$$

(3)

where $n_1$ and $n_2$ correspond to the Avrami exponents, $K_1$ and $K_2$ to the
crystallization rate constants, and $w_1$ and $w_2$ to the weight factor for the
primary and the secondary crystallization, respectively. These weight
factor values provide the relative importance between both crystal-
lizations. At any time, we have $w_1 + w_2 = 1$. For an infinite time, the
total relative crystallinity is the unity that corresponds to the Avrami
model hypotheses [12].

To identify the crystallization kinetic parameters, the Hillier model
has to be fitted to the relative crystallinity calculated from the in-
tegration of crystallization heat flows measured using differential
scanning calorimetry (DSC):

$$\alpha(t) = \frac{\int_0^t Q(t) dt}{\int_0^\infty Q(t) dt}$$

(4)

where $Q(t)$ is the heat flow measured at time $t$, and $t_\infty$ is the time when
the polymer is fully crystallized.

As shown in the literature for other polymers [8,13–15], the inte-
gration of the PEKK crystallization peak is rendered difficult due to
the truncation of the crystallization peak beginning, which has been
attributed to instrumental thermal inertia when switching from the
cooling to the isothermal step (Fig. 1). This phenomenon is more sig-
nificant when the isothermal crystallization temperature decreases or
the polymer has faster crystallization kinetics.

In a previous article [10], we applied the usual method by extra-
polating the beginning of the crystallization peak with a straight line
(dashed line in Fig. 1) until the baseline. However, this method implied
the introduction of a crystallization induction time, which is not con-
sistent with overall crystallization kinetic theories. Secondly, the Av-
rami exponent in this method was found to be close to 2, which is as-
associated with two-dimensional crystallization growth according to
the Avrami theory if we consider instantaneous nucleation. However, this
value of 2 is not consistent with the spherulite entities detected by
microscopic observations as reported in the literature [7,10].

This paper aimed to propose a new methodology to quantify the iso-
thermal crystallization kinetics of PEKK without extrapolating the crys-
tallization peak beginning. We show that this extrapolation could lead to
physically inconsistent values for the Avrami exponent in terms of crys-
talline morphologies. Indeed, microscopic observations of quiescent crys-
tallization put in evidence an instantaneous nucleation and a spherulitic
growth corresponding to an Avrami exponent equal to 3. This new method
will be applied to two PEKK copolymers with different crystallization ki-
etics, namely PEKK 6002 and 7002, to identify their crystallization ki-
etic parameters. Let us recall here that the proposed kinetic modeling can
be applied only for some processing conditions in which strain (elongation
or shear) rate during the crystallization can be neglected such as additive
manufacturing or welding processes. Indeed, high strain rate conditions
mainly promote the nucleation mechanisms by increasing nuclei number
[16]. Finally, TTT diagrams of the relative volume crystallinity will be
built from the overall crystallization kinetic modeling.

2. Experimental

2.1. Materials

The PEKK homopolymer is prepared using diphenyl ether (DPE) and
terephthalic acid (T) (Fig. 2a). Terephthalic acid with para phenyl links
can be substituted by isophthalic acid (I) with meta phenyl links
(Fig. 2a) and form copolymers comprising two different isomers, namely
terephthaloyl (Fig. 2a) and isophthaloyl isomers (Fig. 2b). These isomers can form two different diads: TT diads compounded with
two terephthaloyl isomers and TI diads compounded with one ter-
ephthaloyl isomer and one isophthaloyl isomer.

The PEKK used in this study is provided by Arkema and referenced
as PEKK 6002 and 7002. The ratios of terephthalic acid with para
phenyl links and isophthalic acid with meta phenyl links are 60/40 and
70/30 for PEKK 6002 and 7002, respectively. The two PEKK grades
have an average weight (Mw) and number average molecular mass (Mn)
of about 70 kg.mol$^{-1}$ and 30 kg.mol$^{-1}$, respectively. Glass transition
temperatures of both PEKKs are measured at around 155°C, while the
melting temperatures for PEKK 6002 and 7002 are 305°C and 332°C,
respectively, using DSC with a heating stage of 10°C/min.

2.2. Differential scanning calorimetry (DSC)

Isothermal crystallization analyses are carried out using TA
Instruments Q2000 with granules of about 7–8 mg. All specimens are first heated at 10°C.min$^{-1}$ from room temperature to 360°C for PEKK
6002 and 380°C for PEKK 7002 for 5 min. These temperatures are above the PEKK equilibrium melting temperatures ($T_{m0} = 340°C$ [7])
and erase the thermal history. Specimens are then cooled at
40°C.min$^{-1}$ to annealing temperatures. Annealing temperatures are
maintained for 240 min, and specimens are finally cooled to room
temperature at 40°C.min$^{-1}$. The chosen cooling and heating rates are
high enough to ensure that the polymer does not crystallize before
annealing, while the annealing time is long enough to allow the
polymer to crystallize fully. For all specimens, a heat scan at
10°C.min$^{-1}$ to 400°C is carried out after crystallization to measure
the glass transition, melting temperature, and melting enthalpy induced by
the crystallization cycle.
3. Results and discussion

3.1. Derivative Hillier method

This new identification method based on the Hillier model consists of directly fitting the crystallization heat flow measured by DSC without extrapolating the heat flow at low times and considering only reliable DSC measurements (Fig. 1). The fitting can be done using multi-nonlinear regression available in various numerical tools; we used the “fit” function of the Scilab development tool. Moreover, directly identifying the heat flux by multi-nonlinear regression allows the best baseline to be easily determined according to the model. By deriving Eq. (4), it can thus be written:

\[
\frac{dQ}{dt} = \frac{Q(t)}{\Delta H_c} = \frac{Q(t)}{\Delta H_m}
\]

where \(\alpha\) is the relative crystallinity, \(Q(t)\) the DSC heat flux per mass unit, \(\Delta H_c\) the crystallization enthalpy, and \(\Delta H_m\) the melting enthalpy after crystallization, which was obtained by rapid heating to hinder any fusion or recrystallization process.

The derivative of the primary crystallization kinetic equation (Eq. (2)) can be expressed as follows:

\[
\frac{d\alpha}{dt} = K_1 n_1 t^{n_2-1} \exp(-K_1 t^{n_2})
\]

It can be observed that at time close to 0, the derivative of the primary crystallization kinetic equation (Eq. (6)) tends toward:

\[
\frac{d\alpha}{dt} \propto K_1 n_1 t^{n_2-1}.
\]

Thus, the choice or imposition of curve type to extrapolate the DSC signal will have an influence on the value of the Avrami exponent. If \(n_2\) is equal to equal to 2, for example, the expression of the derivative of the primary crystallization corresponds to the equation of a linear curve with a slope equal to \(K_1 n_2\). This observation is very interesting, because if we assume that the primary crystallization is the main physical phenomenon during the beginning of crystallization, then our extrapolation of the DSC signal by a linear curve primarily explains the Avrami exponent value close to 2 for the primary crystallization found in the first approach [10]. However, this value is inconsistent with microscopic observations previously reported in Refs. [7] and [10]: it can be observed that all crystallite entities have the same size, so instantaneous crystallization can be easily assumed. Moreover, it is difficult to imagine that crystallite entities are not spherulites, and thus according to the Avrami theory [12], the primary crystallization Avrami exponents \(n_2\) could be logically fixed to a value of 3.

The secondary crystallization rate has the following form:

\[
\frac{dQ}{dt} = f(t, t) + \int_0^t \frac{\delta Q(t, t) d\theta}{\Delta H_m}
\]

Consequently, the derivative of the secondary crystallization kinetic equation (Eq. (3)) calculated using Eq. (9) can be expressed by:

\[
\frac{d\alpha}{dt} = K_2 n_2 [1 - \exp(-K_2 t^{n_2})]
\]

Finally, the simplified expression of the derivative Hillier model is, according to our knowledge, given below for the first time:

\[
\frac{d\alpha}{dt} = w_1 K_1 n_1 t^{n_2-1} \exp(-K_1 t^{n_2})
\]

Although this last relation is not useful for fitting, it allows us to understand well the physical meaning of the Hillier model by showing the dependence of the secondary crystallization on the primary crystallization. Nevertheless, this formulation is easily implementable in numerical models.

Finally, we can observe in Fig. 3 that the overall derivative Hillier model fits well with the heat flow and allows us to build the beginning of the crystallization peak truncated by DSC. Besides, we can witnessed the first part of the derivative Hillier model is first associated with the primary crystallization, which shows that the very beginning of the crystallization process corresponds only to the growth of the primary
crystallization. This is then followed by the secondary crystallization growth in relation to the enhancement of the first crystallization stage. The crystallization kinetics of PEKK 7002 is also studied to validate the derivative Hillier model on a PEKK copolymer that crystallizes faster than PEKK 6002. Fig. 4 presents the result of the fitting of the derivative Hillier model (Eqs. (6) and (10)) with the heat flow measured by DSC for PEKK 7002 crystallized at 250°C compared to PEKK 6002 crystallized at 230°C. It is noteworthy the crystallization kinetic for PEKK 6002 is not complete after 13 min, especially the secondary one which is more visible in Fig. 3a. The same primary crystallization Avrami exponent (n1 = 3) as PEKK 6002 is chosen for PEKK 7002 regarding the optical microscopic observations. The same secondary crystallization Avrami exponent (n2 = 1) as PEKK 6002 is also used corresponding to the best fit of the derivative Hillier model. The chosen crystallization temperatures correspond to the fastest temperatures for the crystallization kinetics of PEKK 6002 and 7002. It can be observed that even if the crystallization peak for PEKK 7002 is very narrow compared to PEKK 6002 (Fig. 4), the derivative Hillier model fits well with the experiments and allows us to rebuild the crystallization peak beginning.

3.2. Hillier parameter modeling

Following the general approach reported in the literature for nucleation and crystallization growth, the crystallization rate constants (K1 and K2) can be expressed as a function of the initial number of potential nuclei (N0) and crystal growth rate (G) depending on the crystallization dimensionality and nucleation mode. For primary crystallization, shown to have three-dimensional crystallization growth with an instantaneous nucleation, the crystallization rate constant can be written as:

\[ K_1 = \frac{4}{3} \pi N_{01} G_1^3 \]  

where N01 is the initial number of potential nuclei and G1 the crystallization growth rate for primary crystallization.

For secondary crystallization, shown to have one-dimensional crystallization growth with instantaneous nucleation, the crystallization rate constant can be written as:

\[ K_2 = N_{02} G_2 \]  

where N02 is the initial number of potential nuclei and G2 the crystallization growth rate for secondary crystallization.

According to the Hoffmann and Lauritzen theory [17–19], crystal growth can be expressed by:

\[ G_i(T) = G_{0i} \exp \left( -\frac{U^*}{R(T - T_m)} \right) \exp \left( -\frac{K_{gi}}{T \Delta f} \right) \]  

where G0i is a pre-exponential factor independent of temperature. The first exponential term contains the contribution of the diffusion process to the growth rate, where U* is the activation energy of the molecular transferring through the melt crystal interface, T∞ is the temperature below which diffusion stops (T∞ = Tg-30 K) with Tg = 155°C, and R is the gas constant.

The second exponential term is the contribution of the nucleation process, where Kgi is the activation energy of nucleation for a crystal of critical size, AT is the degree of supercooling (AT = Tm0-T) with Tm0 as the equilibrium melting temperature, and f is a correction coefficient for the temperature dependence of the melting enthalpy (f = 2T / (Tm0 + T)). The index i for Gi, G0i, and Kgi is equal to 1 for primary crystallization and 2 for secondary crystallization.

Finally, the primary crystallization rate constant can be written as:

\[ K_1(T) = K_{01} \exp \left( -\frac{3 U^*}{R(T - T_m)} \right) \exp \left( -\frac{3K_{01}}{T \Delta f} \right) \]  

Fig. 3. Differential scanning calorimetry thermograms of neat poly(ether ketone ketone) 6002 crystallized from the melt at (a) 230°C and (b) 200°C with the fitting of the derivative Hillier model (solid line) and primary (dash curve) and secondary crystallization (dash-dot curve) modeling.

Fig. 4. Comparison of the fitting of the derivative Hillier model for neat poly(ether ketone ketone) (PEKK) 6002 and 7002.
And the secondary crystallization rate constant can be written as:

\[
K_2 = K_{02} \exp \left( -\frac{U^*}{R(T - T_m)} \right) \exp \left( \frac{K_{\alpha2}}{TAf} \right)
\]

(18)

with the pre-exponential factors \( K_{02} = \frac{4}{7} \tau N_{02} G_{02} \) and \( K_{\alpha2} = N_{02} G_{02} \) independent of temperature.

Regarding the evolution of the primary crystallization weight factor \( w_1 \) with the crystallization temperature (Fig. 6), it was chosen to model \( w_1 \) by a linear equation:

\[
w_1(T) = a_1 T + b_1
\]

(19)

where \( a_1 \) and \( b_1 \) are two constants independent of temperature.

The primary crystallization weight factor \( w_1 \) for PEKK 6002 and 7002 is plotted as a function of temperature in Fig. 6 with the fitting of the linear model (Eq. (18)). Results for \( a_1 \) and \( b_1 \) are presented in Table 1. We observed that for PEKK 6002, \( w_1 \) decreases with temperature, knowing that \( w_1 + w_2 = 1 \) (see eqs. (1)–(3)), it shows that the formation of the secondary crystallization is promoted by the low...
degree of supercooling. This observation is also reported by other authors [9,22], with an increase in the first endothermic peak, which occurs 10°C above the annealing temperature attributed to the melting of the secondary crystallization. In fact, for high annealing temperatures, the diffusion process is very important, with a high mobility of chains allowing the crystalline phase to be enhanced. For PEKK 7002, $w_1$ seems to be quasi-constant as a function of temperature with a value of around 0.78. PEKK 7002 wt factors are higher than for PEKK 6002, which could be attributed to a more organized crystallization process that leaves less room for the growth of secondary crystallization.

### 3.3. Time-temperature-transformation (TTT) diagrams

As the relative crystallinity of PEKK 6002 and 7002 depending on time can be determined for any temperatures with the modeling of the Hillier parameters, we built TTT diagrams of the relative volume fraction crystallinity for the overall crystallization for PEKK 6002 (Fig. 7a) and 7002 (Fig. 7b). This kind of representation allows the crystallinity of the material to be determined for any isothermal crystallization process as well as the corresponding crystallinity ratios of each crystallization mechanism. As expected, crystallization kinetics are fastest around 240°C for PEKK 6002 and 245°C for PEKK 7002. The TTT diagrams show the very fast crystallization kinetics of PEKK 7002 compared to PEKK 6002. For example, it takes 10 min for PEKK 7002 to fully crystallize at 240°C, whereas only about 50% of PEKK 6002 crystallizes in the same conditions.

### 4. Conclusion

The modeling of PEKK crystallization kinetics proves difficult due to a significant secondary crystallization, which has to be taken into account in the process modeling. Furthermore, to typically assess the crystallization enthalpy based on the DSC thermogram, the integration of the crystallization heat flow implies an extrapolation of the beginning of isothermal crystallization stage. If the extrapolation is done using a straight line, this generally involves a truncation of the beginning of all isothermal crystallization peaks. As a result, this truncation leads to underestimating the crystallization enthalpy value, constraining the Avrami exponent to a value close to 2, and sometimes introducing an induction time to fit the data with overall crystallization kinetic modeling.

To solve this problem, we established a new methodology from the derivative of the Hillier isothermal crystallization kinetic model, which can be directly fitted on the crystallization heat flux measured by DSC. The Hillier model allows us to deconvolute the contribution of the primary and secondary crystallization processes. This approach has been successfully applied to PEKK 6002 and 7002 for isothermal crystallizations from the glassy state and from the melt between 200°C and 300°C. PEKK 7002 was shown to crystallize much faster than PEKK 6002, with rapid crystallization kinetics around 245°C. According to the linear modeling of the primary crystallization weight factor $w_p$, the secondary mechanism was found to be enhanced for a low degree of supercooling due to the high diffusion process for PEKK 6002, whereas it was observed to be constant for PEKK 7002. Finally, the isothermal TTT diagrams for crystallization built for PEKK 6002 and 7002 provide a useful tool for PEKK processing.

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### References


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Fig. 7. Time-temperature-transformation diagram of the relative crystallinity of poly(ether ketone ketone) (PEKK) (a) 6002 (b) and 7002 crystallized from the melt.


