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A STEPWISE METHOD FOR THE CHARACTERIZATION OF NON-ISOTHERMAL CRYSTALLIZATION KINETICS OF POLY(ETHER ETHER KETONE) AT PROCESSING-RELEVANT COOLING RATES

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Abstract: *Isothermal and non-isothermal crystallization kinetics of PEEK are investigated experimentally using fast scanning calorimetry. A stepwise method to derive the kinetics from interrupted crystallization tests is introduced. The evolution of crystallinity as a function of time is evaluated from the variation of specific heat capacity to avoid taking into account melt-recrystallization phenomena when integrating the melting enthalpy. This experimental work allows the construction of a continuous cooling transformation diagram, at cooling rates close to those of industrial processes.*

Keywords: Crystallization kinetics ; Fast scanning calorimetry ; PEEK

1. Introduction

The use of thermoplastic composites is expanding in the transportation industry, particularly in response to stricter emission regulations that make it necessary to lighten structures. To achieve the production rates required by this high-volume market, forming and assembly processes that allow short cycle times (injection, thermoforming, thermoplastic welding) are used. These processes, which are generally non-isothermal, are based on processing above the melting temperature of the thermoplastic matrix. The microstructure of the final part depends on the cooling conditions from the molten state. The characterization of the crystallization of these semi-crystalline polymers is necessary to understand the relationship between process parameters and final part properties. In thermoplastic welding processes for example, the interaction between chain diffusion at the interface and crystallization can lead to significant variations in the quality of adhesion as a function of the imposed temperature cycle.

Poly(ether ether ketone) (PEEK) is a high performance semi-crystalline thermoplastic polymer with excellent mechanical properties and good thermal stability, used in particular for structural applications in the aerospace and automotive industries. Crystallization of PEEK under isothermal and non-isothermal conditions at rates up to 90K/min has been the subject of numerous differential scanning calorimetry (DSC) studies [2,3,4]. However, no study presents results under non-isothermal conditions for cooling rates close to those of industrial processes (10-100K/s).

2. Experimental protocol

2.1 Fast scanning calorimetry (FSC)

Fast differential scanning calorimetry (FSC) is a recent extension of standard differential calorimetry, allowing to reach heating and cooling rates up to 10^6 K/s [5]. This technique allows the investigation of very fast phase change phenomena, which are often inaccessible for conventional devices. The tests were carried out using a power-compensated Mettler Toledo Flash DSC1 instrument, equipped with UFS1 chip sensors allowing a heating rate up to 10000K/s and cooling up to 5000K/s.

The study material is a low viscosity PEEK grade developed by Solvay and supplied in pellet form. After drying, a small sample of the material is cut from the pellet with a scalpel, positioned in the center of the sensor measurement area and melted at a rate of 10K/s to allow good thermal contact with the chip prior to further analysis (Figure 1). A relatively high sample mass compared to other literature studies (about 500ng) is used to ensure that the crystallization phenomena are representative of those of the bulk material.

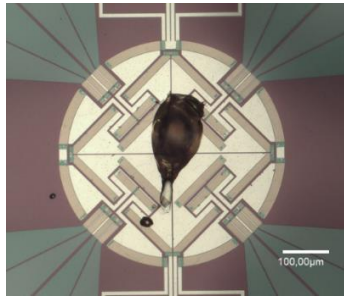


Figure 1 – PEEK sample on a UFS1 chip

2.2 Stepwise method for the characterization of crystallization kinetics

2.2.1 Isothermal crystallization

Preliminary tests have shown that the characterization of crystallization kinetics directly from the integration of the crystallization peak during cooling is not possible due to a low signal to noise ratio, i.e. the crystallization heat flow is too low to be directly measured. A discrete method based on a sequential approach is therefore applied to characterize the crystallization. The isothermal protocol, developed in a previous study [6] and described in Figure 2a., consists in (1) erasing the thermal history of the material by heating above the melting temperature, (2) cooling at high rate (2000K/s, which is shown to be sufficient to ensure that no crystallization takes place during cooling) to the isothermal crystallization temperature, (3) performing an isothermal step of a defined duration, (4) cooling at 2000K/s to room temperature and (5) heating at 2000K/s to 380°C. This protocol is repeated by varying the time and temperature of the isothermal step. Isothermal crystallization is studied here between 160°C and 320°C (i.e. a temperature range between $T_g+10^\circ\text{C}$ and $T_m-20^\circ\text{C}$ approximately), and for step times varying between 0.01s and 3600s.

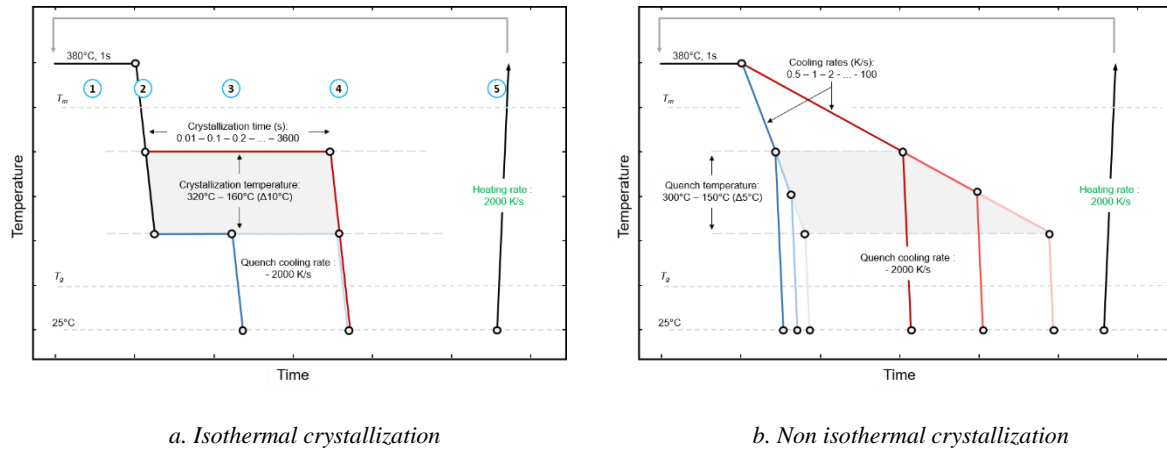


Figure 2 – FSC temperature cycle

2.2.2 Non-isothermal crystallization

The discrete method presented above is extended to study non-isothermal crystallization (Figure 2b.). After the thermal history erasure step, the sample is cooled at the rate of interest to a fixed temperature T_{quench} before quenching the resulting microstructure at 2000K/s. The sample is then heated at 2000K/s to melt the crystals formed during cooling. The test is repeated for several values of T_{quench} (between 150°C and 300°C) and several values of cooling rate (from 0.5 to 100K/s) to discretely reconstruct the crystallization kinetics.

3. Experimental results

3.1 Isothermal crystallization

An example of curves corresponding to the raw heat flux measured during the heating step following isothermal crystallization, obtained by varying the dwell time for a temperature of 220°C, is shown in Figure 3.

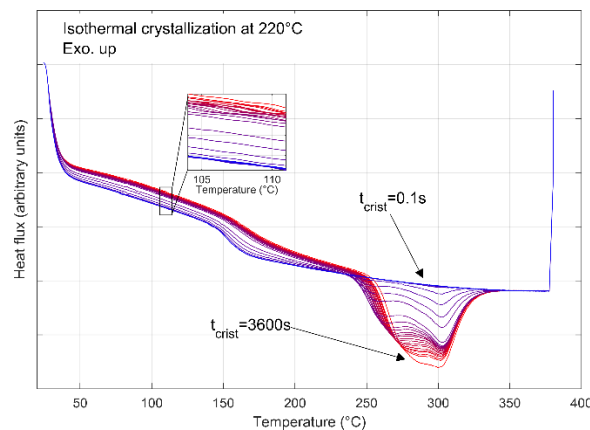


Figure 3 – Heat flux during heating following isothermal crystallization at 220°C varying dwell times

The curves show a marked transition near 160°C, corresponding to the glass transition of the amorphous phase, followed by a melting peak of variable amplitude depending on the duration of the isothermal crystallization stage. Two distinct melting peaks are apparent; this double melting phenomenon, classical for PEEK, corresponds to the melting of two crystal populations.

However, it has been shown in the literature that the peak corresponding to the higher melting temperature is due to a melt-recrystallization phenomenon during heating [5,6]: as soon as the crystalline phase starts to melt, the oriented chains can recrystallize into more stable lamellae. This phenomenon occurs continuously until recrystallization is no longer possible. Therefore, the method consisting in measuring the crystallization generated during the isothermal stage from the direct integration of the global melting peak is not directly applicable: this peak being the sum of the melting enthalpy associated to the crystals generated during the isotherm, and the melting/recrystallization enthalpy. Moreover, the phenomenon being continuous, the deconvolution of the melting peaks which would allow to consider only the enthalpy associated to the first peak is also not adapted.

To avoid the error associated with taking into account the melt-recrystallization, the direct measurement of the variation of the specific heat capacity of the sample is proposed. The heat capacity depends linearly on the crystallinity ratio α by equation (1), and the heat flux measured by calorimetry is proportional to the specific heat capacity (equation 2).

$$C_p^{tot}(\alpha, T) = (1 - \alpha)C_p^{am.}(T) + \alpha C_p^{cr.}(T) \quad (1)$$

$$\phi = \frac{dH}{dt} = m C_p^{tot} \frac{dT}{dt} \quad (2)$$

The new approach is therefore to observe the variation of the heat flow ϕ measured by FSC during heating after isothermal crystallization as a function of the step time, and for a temperature below the glass transition temperature so as to prevent any modification of the crystalline structure. In practice the observed variation is averaged over the range 105°C - 110°C (see inset in Figure 3). Figure 4 shows the evolution of the relative crystallinity of the sample as a function of time, calculated with the two methods presented (integration of the global melting peak and variation of the specific heat capacity) and for plateau temperatures between 230°C and 290°C.

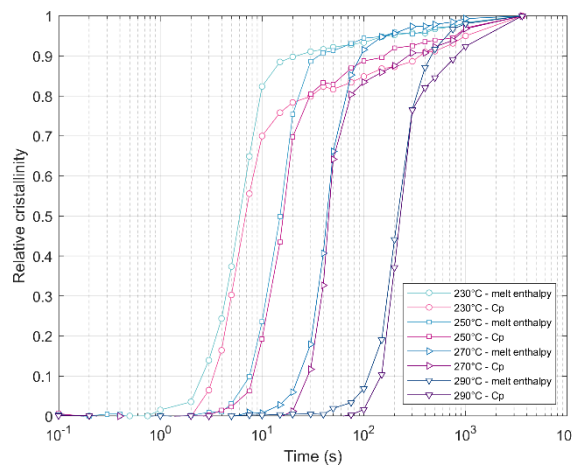


Figure 4 – Relative cristallinity evolution measured from the total melting enthalpy and specific heat capacity

The curves obtained (independently of the method) show at first a sigmoidal evolution of the crystallinity attributed to the primary crystallization, then a linear evolution with the logarithm of time attributed to the thickening of the crystalline lamellae (secondary crystallization). Both

approaches lead to equivalent half-crystallization times. The approach based on the direct integration of the melting peak leads to an overestimation of the crystallinity, associated with the enthalpy of fusion/recrystallization.

3.2 Non-isothermal crystallization

An example of curves corresponding to the raw heat flux measured during the heating step following non-isothermal crystallization, obtained by varying the temperature before quenching, is shown in Figure 5 for a cooling rate of 5K/s. We can observe in the same way as for the isothermal crystallization a double melting peak whose enthalpy increases with the decrease of the temperature before quenching.

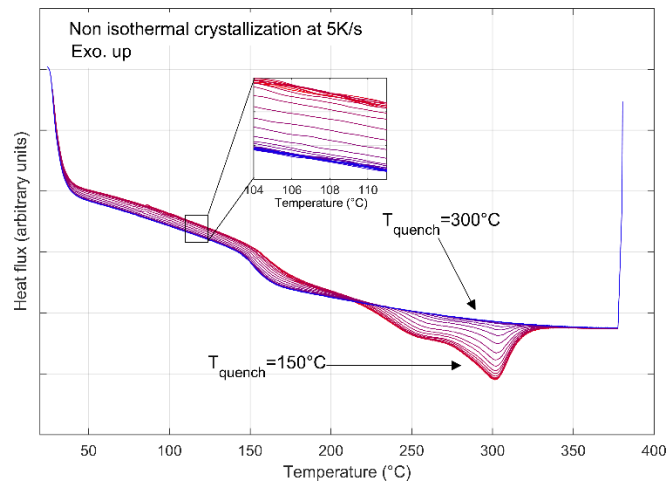


Figure 5 – Heat flux measured during heating after non-isothermal crystallisation at 5K/s interrupted at different temperatures

The double melting peak is also due to a melting/recrystallization phenomenon during heating. Therefore, the analysis of the crystallization kinetics is performed from the observation of the evolution of the specific heat as presented previously. The evolution of the maximum relative crystallinity under non-isothermal conditions is presented in Figure 7 as a function of the cooling rate. A marked decrease in crystallinity is observed for cooling rates above 10K/s with complete amorphization above 100K/s. This validates the choice of a cooling rate of 2000K/s in the protocol employed as adequate to quench the crystalline microstructure.

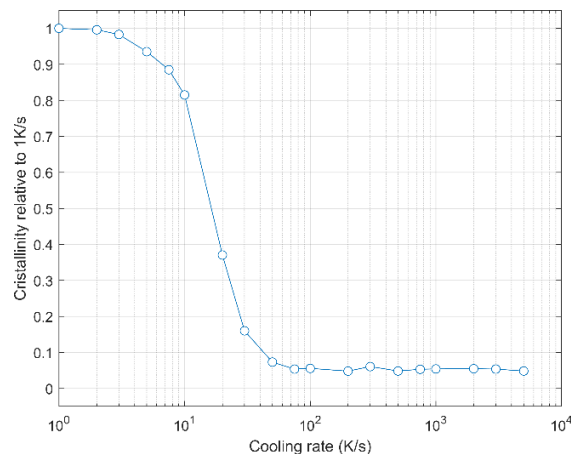


Figure 6 – Relative cristallinity as a function of cooling rate

The evolution of the specific heat capacity as a function of temperature for the different cooling rates evaluated shows a classical sigmoidal pattern of non-isothermal crystallization. The derivation of the curves allows to reconstruct the evolution of the endothermic heat flux related to the crystallization (Figure 7). The proposed experimental protocol thus allows to obtain the shape of the crystallization peak, which is not accessible in FSC by direct method, and this for cooling rates up to 5000 times higher than in DSC. We observe a decrease in the amplitude of the crystallization peak with the increase of the cooling rate, as well as a shift of the extremum towards lower temperatures: from 270°C at 0.5K/s to 220°C at 15K/s.

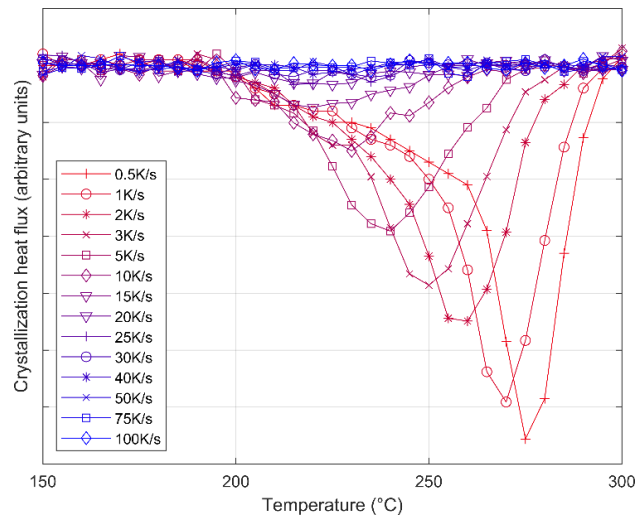


Figure 7 –Crystallization heat flux obtained from the stepwise method

This experimental campaign also allows to edit a CCT process diagram (continuous cooling transformation diagram, Figure 8) of PEEK, in a range of cooling rates corresponding to the industrial forming processes. This diagram makes it possible to determine the relative crystallinity of the material under non-isothermal conditions, and thus to define the adequate cooling rates according to the desired crystal structure. This graph shows that the crystallization phenomenon takes place mainly between 270°C and 200°C, temperature below which the molecular mobility is too limited. An analytical model to describe the non-isothermal crystallization kinetics of PEEK from the experimental results obtained remains to be developed.

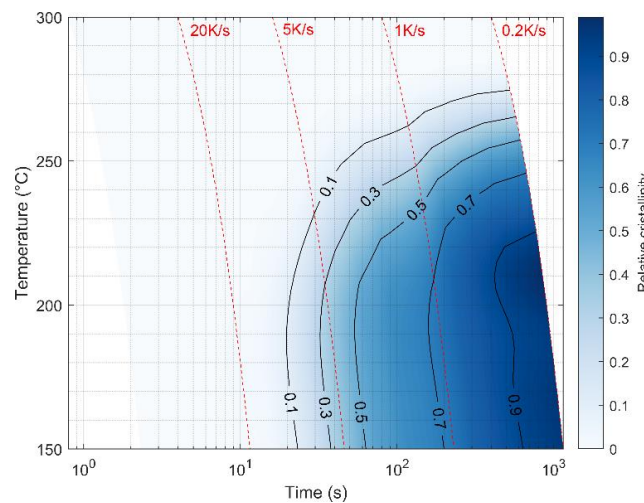


Figure 8 – CCT diagram of PEEK

4. Conclusion

This experimental work has allowed the characterization of isothermal and non-isothermal crystallization kinetics of PEEK by rapid differential scanning calorimetry. The protocol based on the analysis of interrupted crystallization tests allows to override the relatively slow crystallization mechanisms of the studied material. The use of the specific heat capacity as a measure of crystallinity also allows to avoid the error induced by taking into account melt-recrystallization phenomena when integrating the melt enthalpy.

Results obtained for isothermal crystallization show a secondary crystallization mechanism with a logarithmic evolution in time, attributed to lamellae thickening. Interrupted non-isothermal crystallization tests provide for the first time a description of the crystallization kinetics of PEEK in a range of cooling rates comparable to industrial processes. A model to describe the non-isothermal kinetics is under development. Moreover, the proposed experimental methodology is currently used to extend the study to the degradation of the material, in order to characterize the impact of thermo-oxidation phenomena on the ability of PEEK to crystallize.

5. References

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