

Thermal treatment influence on the crystalline microstructure of compacted Polytetrafluoroethylene

G. Guenoun^{a,b,c}, N. Schmitt^a, G. Regnier^b

a. LMT, ENS Paris-Saclay, CNRS, Université Paris-Saclay

61, avenue du Président Wilson, 94235 Cachan, France

b. PIMM, ENSAM, CNRS, CNAM

151 boulevard de l'Hôpital, 75013 Paris, France

c. Saint-Gobain Recherche, 39 Quai Lucien Lefranc, 93300

gabriel.guenoun@ens-cachan.fr

Résumé :

La cristallisation anisotherme du PTFE est étudiée au moyen de calorimétrie différentielle à balayage (DSC). Une attention particulière est portée sur l'existence d'une seconde cristallisation et de son influence. Les résultats indiquent que la cinétique de cristallisation anisotherme du PTFE peut être décrite par le modèle d'Hillier retranscrit dans le formalisme d'Ozawa.

Abstract :

The anisothermal crystallization behavior of PTFE is investigated using differential scanning calorimetry (DSC). Special attention is paid on the existence of a secondary crystallization. Results show that anisotherm crystallization kinetics may be simulated by a modified Hillier model based on Ozawa's formalism.

Key words : Polytetrafluoroethylene (PTFE), crystallization, anisotherm, differential scanning calorimetry (DSC), thermal treatment, Ozawa, Hillier

1 Introduction

Polytetrafluoroethylene has some very interesting properties such as low friction coefficient or high thermal stability. However, its processing is rather difficult due to its high viscosity at molten state. One manufacturing process consists in sintering parts of compacted PTFE powder^[1]. During such a thermal cycle, PTFE is cooled to different cooling rates at different locations inside large parts due to thermal gradient. This paper aims to understand the crystallinity evolution of PTFE with different cooling rates in order to capture the microstructure evolution of the PTFE during sintering thereafter.

2 Experimental

PTFE commercial grade A was used for this study. Differential scanning calorimetry (DSC) was performed using a DSC Q1000 from TA instruments at various cooling rates ranging from 1 to 32 K/min under constant nitrogen flow. Samples between 4 mg and 40 mg were heated at 370 °C before cooling.

3 Overall crystallization kinetics model

Crystallization kinetics of polymers is usually studied under isothermal conditions because model identification is then easier. Experiments performed at different temperatures enable to capture the temperature dependency. Avrami model^[2] is a very robust crystallization model. The relative crystallinity α is given by:

$$\alpha(t) = 1 - \exp\left(-K(T)t^n\right) \quad (1)$$

where t is the time, $K(T)$ is the crystallization growth rate and n is an integer related to the dimensional order of crystal growth.

However, equation 1 describes only the crystallinity evolution for isothermal crystallization, and PTFE crystallizes very rapidly and in a quite narrow range of temperature which makes it difficult to characterize easily under isothermal conditions. Therefore, non isothermal crystallization has been investigated.

Ozawa adapted Avrami model to anisothermal crystallization^[3] at a constant cooling rate ϕ with $\phi = \frac{dT}{dt}$:

$$\alpha(T) = 1 - \exp\left(-\frac{k(T)}{\phi^n}\right) \quad (2)$$

where $k(T)$ is Ozawa's crystallization growth rate that can be obtained from Avrami's crystallization growth rate with Nakamura's equivalence^[4] : $K(T) = \left(\frac{dk^{1/n}}{dT}\right)^n$.

From these relations, Avrami's crystallization growth rate can be deduced:

$$K = \frac{\phi^{n-1}}{1-\alpha} \frac{d\alpha}{dt} \quad (3)$$

4 Results and discussion

DSC scans were performed on PTFE samples at different cooling rates (1, 1.5, 2, 4, 6, 8, 10, 16 and 32 K/min) from 370 °C to -5 °C.

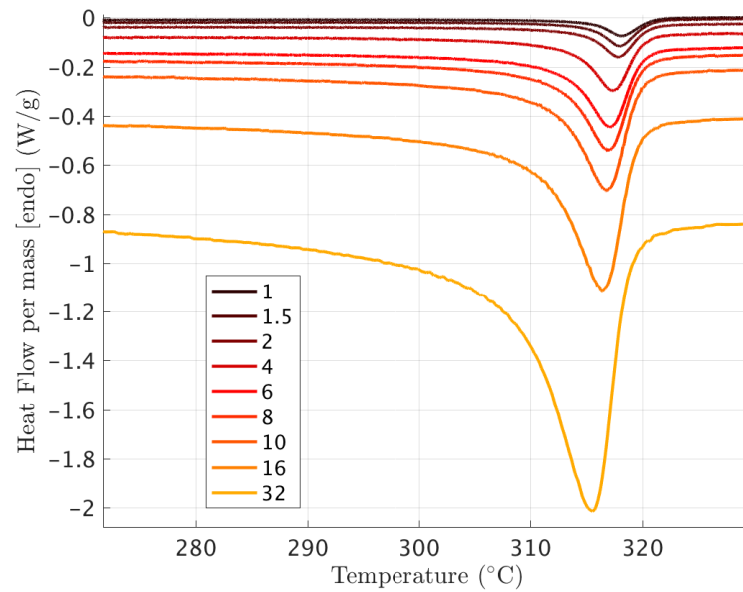


FIGURE 1 – DSC scans of the crystallization of PTFE for different cooling rates (°C/min).

Crystallization peaks were integrated in order to extract the relative crystallinity α as a function of the temperature for each cooling rate, using the following relation: $\alpha(T) = \frac{\int_0^T Q dT}{\int_0^\infty Q dT}$ where $Q(T)$ is the heat flow per mass that can be read in Figure 1.

From these curves, the parameter n was determined by plotting $\log(-\ln(1 - \alpha))$ as a function of $\log(\phi)$ for different temperatures in Figure 2. n that was measured from the slope of those curves. n is ranging between 0.65 and 0.85. These results are consistent with those obtained by Ozawa^[5] and can be interpreted as a one dimensional crystal growth ($n = 1$). A difference between this value and an integer could be explained by the existence of other mechanisms and shows the limit of this model.

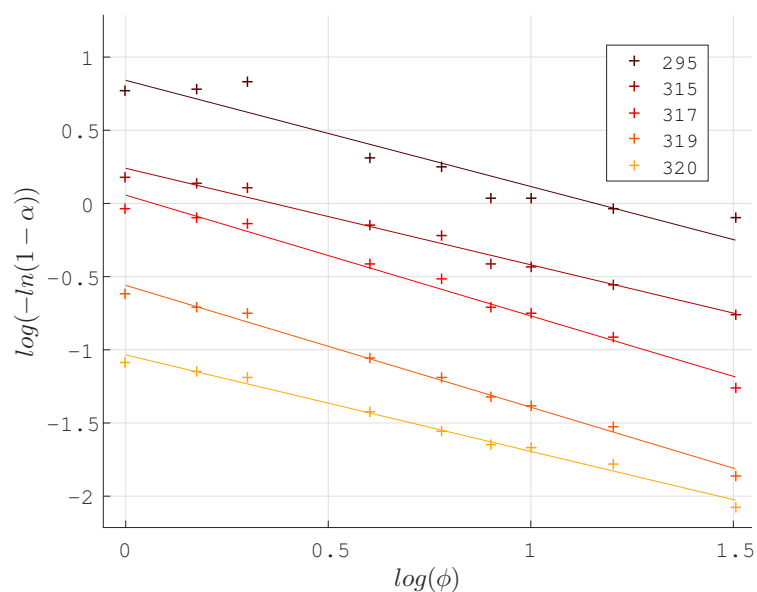


FIGURE 2 – Plots of $\log(-\ln(1 - \alpha))$ as a function of $\log(\phi)$ for different temperatures $T(^\circ\text{C})$.

Ozawa showed in his article^[5] that Avrami's crystallization growth rate can be extracted from the calculation of α using equation 3 with $n = 1$: $K = \frac{1}{1-\alpha} \frac{d\alpha}{dt}$. Figure 3 shows this quantity for different cooling rates. The curves do not overlap which suggests that this model cannot describe the crystallization kinetics of PTFE, and emphasizes the existence of a secondary crystallization mechanism.

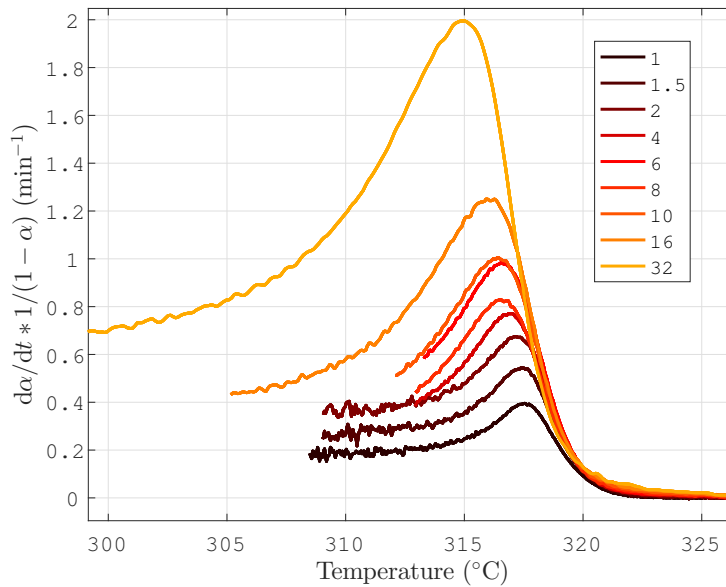


FIGURE 3 – Plots of $\frac{1}{1-\alpha} \frac{d\alpha}{dt}$ as a function of the temperature for different cooling rates.

In order to take into account both primary and secondary crystallizations, Hillier proposed a model^[6] in which a secondary crystallization grows from the primary crystals:

$$\alpha(t) = w \left(1 - \exp(-K_1 t^{n_1}) \right) + (1-w) \int_0^t (1 - \exp(-K_1 \theta^{n_1})) \frac{d}{dt} \left(1 - \exp(-K_2 (t-\theta)^{n_2}) \right) d\theta \quad (4)$$

where $w(T)$ is the weight of the primary crystallization compared to the secondary one, K_1 and K_2 are respectively Avrami's crystallization growth rates for the primary and for the secondary crystallization and, n_1 and n_2 their dimensions of growth. This equation is valid for isothermal crystallization but it can be adapted to anisothermal crystallization using Ozawa's formalism.

This model is very difficult to fit for anisothermal crystallization because of the number of parameters to determine and their coupling with temperature. However, using this model with a constant weigh parameter $w = 0.9$ and a weak secondary crystallization, $\frac{1}{1-\alpha} \frac{d\alpha}{dt}$ is simulated in Figure 4. The Avrami crystallization growth rate for primary crystallization is chosen in order to fit the beginning of the curves that does not change during cooling in Figure 3, and with the parameters found by Wang^[7] for a Hoffman-Lauritzen growth rate^[8]. The variation with the cooling rate is in agreement with what has been observed in the experiments confirming the existence of a secondary crystallization.

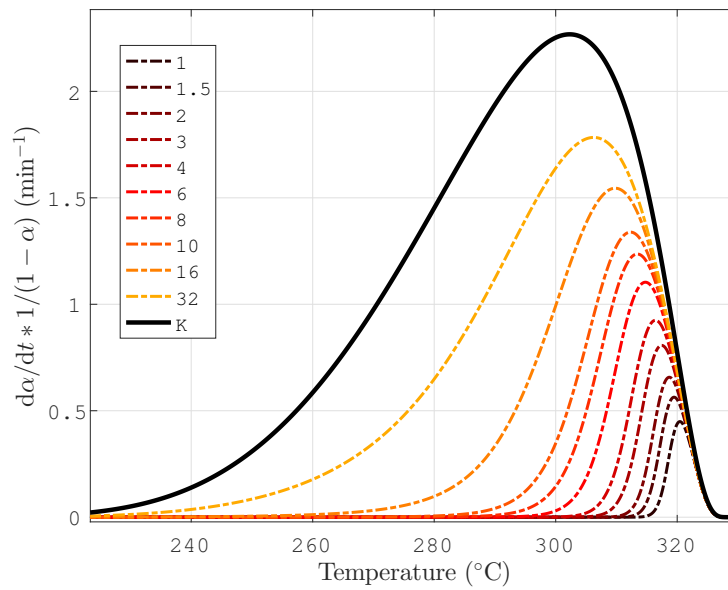


FIGURE 4 – Simulations of $\frac{1}{1-\alpha} \frac{d\alpha}{dt}$ as a function of the temperature for different cooling rates obtained with Hillier's crystallization model for $w = 0.9$.

5 Conclusions and perspectives

This paper aims to exhibit the strong influence of a secondary crystallization mechanism during anisothermal crystallization of PTFE. It also makes a first step in its modelling using a modified Hillier model for anisothermal crystallization.

Futur work will be made on the overall modelling of the evolution of the PTFE crystalline microstructure during thermal treatments and a special attention will be paid to characterize crystals orientation which can lead to anisotropic mechanical properties.

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