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Experimental and Modeling of Isothermal crystallization of PEEK matrix and C/PEEK composites with application of parallel Avrami Model

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Abstract

Isothermal crystallization kinetics of neat PEEK (Poly(Ether-EtherKetone)) and carbon fibers reinforced PEEK (30% in mass) were studied and modeled. A differential scanning calorimeter was used to monitor heat flow during isothermal crystallization between 300°C and 310°C. PEEK thermoplastic polymer exhibits a particular crystallization that induces a double melting peak after isothermal crystallization that is described by a model that features two competing nucleation and growth mechanisms. Concerning neat PEEK and reinforced PEEK respectively, the first mechanism is a primary crystallization with Avrami's coefficient of 2.1 (resp. 3.2), the second is interlamellar crystallization with Avrami's coefficient of 1.7 (resp. 2.7). Kinetics parameters are identified, and confirm the influence of fibers on crystallization kinetic.

1 Introduction

General tend in aeronautical industry is to move toward more eco-efficient and REACH compatible materials and processes. One of the main topic concerns the composite material technology, where the classical thermoset based autoclave manufacturing is progressively replaced by out of autoclave processes and thermoplastic based materials. As a matter of fact this later class of materials has no requirements for low temperature conservation of raw materials and allows rapid manufacturing processes.

Among the different thermoplastics, Poly-Ether-EtherKetone (PEEK) corresponds to the one that allows to get the best mechanical properties. Nevertheless such high properties can only be obtained if the level of crystallinity is high enough (typically more than 35% in mass), and in particular if crystallization occurs at high temperature (isothermal conditions) or at low cooling rates. In such conditions the material exhibits a double melting peak, where the main one corresponds to the classical theory of nucleation and subsequent crystal growth, very well described by the classical macroscopic models [1, 2]. If secondary melting peak origin is still discussed, most of the authors agree that it may correspond to a secondary crystalline phase [3-6].

It is therefore of prime importance to develop models able to predict this complex crystallinity rate of PEEK for material process optimisation purposes. Velisaris and Seferis [7] first proposed a model for isothermal crystallization of PEEK combining two Avrami models in order to take into account two competing crystallization processes for neat PEEK.

This paper investigates the effect of adding carbon fibres on the crystallization behaviour of neat PEEK and their influence on the parameters of a specific crystallisation model, based on generalized Avrami form [8] during isothermal crystallization conditions.

2 Materials and testing methods

The neat material under investigation is a (Poly-Ether-Ether-Ketone) PEEK provided by Victrex as a powder with the reference 151G. The reinforced PEEK is a 150Ca30 compound, supplied by Victrex to with 151G PEEK reference and 30% of short carbon fibers. The crystallization kinetics were studied by Differential Scanning Calorimetry (DSC) with a Perkin-Elmer 8000 equipment. The DSC sealed caps were prepared with 1.5 to 2 mg of PEEK powder and, in order to start the cooling from a nuclei-free melt, the samples were systematically heated from room temperature to 400°C and held for 5 minutes in the molten state.

After quickly cooling the sample at 200°C.min⁻¹, samples are kept at T_{iso} for 15 min and cooled again quickly to room temperature. All the crystallized samples were subjected to a heating ramp of 10°C.min⁻¹ from room temperature to 400°C in order to determine the mass fraction crystallinity in considering a reference enthalpy of fusion of 130J.g⁻¹ [8]. The transformation rate was assessed from the crystallization heat flux by using the partial area method.

2 Isothermal crystallization results

2.1 Neat PEEK isothermal crystallization

Five isothermal temperatures were investigated between 300°C and 310°C, considering 3 samples per temperature. The relative mass crystallinity is plotted as a function of time in Figure 1 for 3 different temperatures. It can be seen that PEEK crystallization is a continuous process, and if its general sigmoidal shape is characteristic of an classical nucleation and growth process, its non symmetry confirms the unusual crystallization behaviour of PEEK. Crystallization duration depends on testing temperature: for an equivalent transformation rate, the lower the temperature, the higher the crystallization kinetic is, i.e. if crystallization at 310°C occurs within 6 minutes this duration drops to less than 1 minute at 300°C.

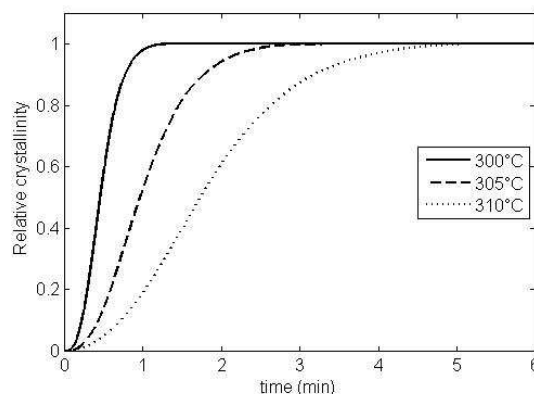


Figure 1. Isothermal crystallization kinetics for neat PEEK

Figure 2 illustrates the endothermic thermograms of polymer melting measured after isothermal crystallization at, 305 and 310°C : the PEEK fusion systematically displays a double peak already reported in the literature [3, 6, 9, 10]. The main melting peak temperature is 343°C whatever isothermal temperature investigated during the cooling stage. It corresponds to the fusion of the orthorhombic crystalline phase of PEEK and it is assumed to be the main melting temperature [7, 11]. The maximum temperature of the secondary melting

peak, appears at lower temperature. This peak, is consistently 6 to 7°C above the temperature of the isothermal crystallization step. For example, an isothermal crystallization at 310°C induces a secondary melting peak at 317°C.

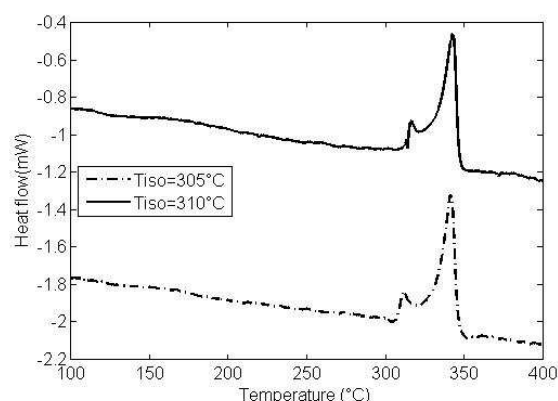


Figure 2. Enthalpy of fusion for neat PEEK crystallized at 305°C and 310°C

Most of the authors agree that this secondary may correspond to a crystalline phase, therefore, this peak must be taken into account when calculating the total degree of crystallinity.

T isotherm (°C)	ΔH (J.g⁻¹)	Standard Deviation	Xm (wt %)
300	47.9	1.6	36.6
302	48.8	2.6	37.5
305	47.1	0.3	36.2
308	47.6	0.8	36.6
310	49.2	0.7	37.8

Table 1. Enthalpies of fusion and crystalline mass fraction for different temperatures

Table 1 summarizes the enthalpy of fusion and the resulting degree of crystallinity obtained for the five different test conditions. It can be seen that, taking into account this double peak insures a large degree of crystallinity, above 34%wt for all investigated test conditions, Moreover, the estimated Standard Deviation of the three different tests is low and confirms the methodology used.

2.2 Carbon fiber reinforced PEEK isothermal crystallization

Similarly five isothermal temperatures were investigated between 300°C and 310°C. In figure 3, the relative mass crystallinity is plotted as a function of time for three different temperatures, and is compared to the crystallization kinetic of neat PEEK at 310°C. As for neat PEEK the sigmoidal shape is characteristic of the crystallization of homopolymer with nucleation and growth process. The time needed for crystallization depends on testing temperature and is less than 4 min. Comparing reinforced PEEK crystallization, it appears that fibers increase the kinetics of PEEK crystallization, as it can be seen on the figure 3 at 310°C

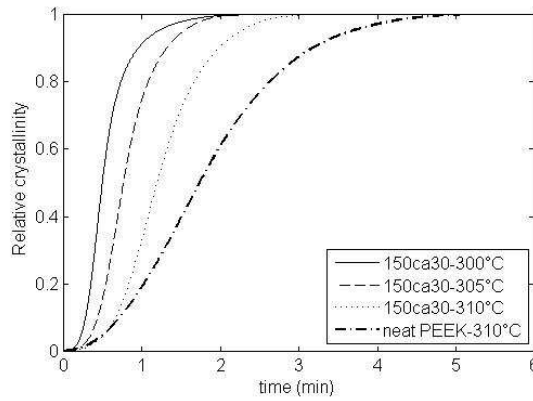


Figure 3. Isothermal crystallisation kinetic of reinforced PEEK and neat PEEK

Figure 4 illustrates the endothermic thermogram of reinforced PEEK measured after two isothermal crystallization step 300°C and 310°C. As for neat PEEK a double melting peak appears, this second melting peak still appears at lower temperature and is consistently 6 to 7°C above the temperature of the isothermal crystallization step (resp. 307°C for an isotherm at 300°C).

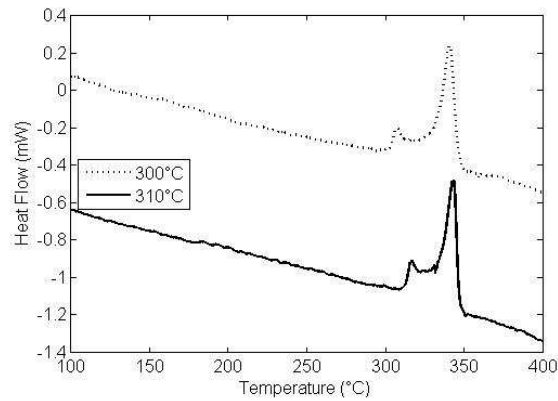


Figure 4. Enthalpy of fusion for reinforced PEEK crystallized at 300°C and 310°C

Table 2 shows the enthalpies of fusion and the mass crystallinity obtained after isothermal crystallization at 300°C, 302°C, 305°C, 308°C and 310°C. Final crystallinity rates always exceed 33% , the maximum is obtained for temperatures below 305°C. Despite a high crystallinity, a difference of 2-3% on final mass crystallinity could be noticed between neat and reinforced PEEK. So, the introduction of 30% carbon fibres has an influence on crystallization kinetics and on the final mass crystallinity.

T isotherm (°C)	ΔH (J.g⁻¹)	X_m (wt%)
300	33.5	36.8
302	32.3	35.5
305	32.4	35.6
308	29.8	33.7
310	31.3	34.4

Table 2. Enthalpies of fusion and crystalline mass fraction for different temperatures

3 Kinetic modeling and identification

3.1 Kinetic model description

The isothermal crystallization kinetics are usually studied using Avrami's law (Eq. 1) where $\alpha(t)$ is the fraction of crystal transformed at time t during crystallization, $X(t)$ is the fraction of crystallization at time t and $X(\infty)$ is the volume crystalline fraction for infinite time at temperature T [12]. Applied to polymers, the exponent n (Avrami exponent) contains some information on the type of nucleation while K characterizes the crystallization growth rate (s^{-1}) and depends on the isothermal testing temperature.

$$\alpha(t) = \frac{X(t)}{X(\infty)} = 1 - \exp(-K * t^n) \quad (1)$$

In order to model isothermal and anisothermal polymer crystallization kinetics a model based on a generalized Avrami form (Equation. (2))[13] was proposed in a previous work [8]. This form allows the expression of a time independent differential evolution equation as seen in equation (3).

$$\alpha(t) = \frac{X(t)}{X(\infty)} = 1 - \exp(-(K * t)^n) \quad (2)$$

$$\dot{\alpha} = (1 - \alpha(t)) * n * K * \ln\left(\frac{1}{1 - \alpha(t)}\right)^{\frac{n-1}{n}} \quad (3)$$

Nevertheless, application of the classical Avrami's model to PEEK don't allow a good representation of crystallization kinetic, in particular for isothermal condition [7, 8, 11, 12].

In order to take into account the contribution of the two complementary mechanisms the total crystallization rate was modeled with Equation 4 where $i=1$ (resp. $i=2$) corresponds to main (resp. minor) crystallization mechanism [8]. Each crystallization process is associated to a weighting factor, respectively w_1 and w_2 , with $w_1 + w_2 = 1$.

$$\dot{\alpha} = \sum_{i=1}^2 w_i * \dot{\alpha}_i = \sum_{i=1}^2 w_i * (1 - \alpha_i) * n_i * K_i * \ln\left(\frac{1}{1 - \alpha_i}\right)^{\frac{n_i-1}{n_i}} \quad (4)$$

3.2 Neat PEEK and carbon fiber reinforced PEEK isothermal model parameters identification

Crystallization model parameters identification is performed with a numerical optimization procedure developed in Matlab[®]; it compares isothermal DSC results with the numerical integration of Equation 4 using Runge-Kutta method. During the optimization only upper and lower bounds were set for w_1 (respectively 1 and 0,5), and four other parameters (n_1 , n_2 , K_1 and K_2) were considered free. Table 3 summarizes the optimization results obtained for the different materials at three temperatures.

For each material configuration the exponents n_1 and n_2 are found constant, thus not influenced by temperature. Concerning neat PEEK, the Avrami exponents for the first and the second mechanism are respectively 2.1 and 1.7. The n exponent characterizes the crystallization type (nucleation and growth), and according to the results, carbon fibers have a strong influence on crystallization indeed Avrami exponent evolve toward 3.2 and 2.7.

	Neat PEEK	150ca30	Neat PEEK	150ca30	Neat PEEK	150ca30
Temperature (°C)	300		305		310	
K_1 (T)	$3.1 \cdot 10^{-2}$	$3.1 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$	$4.3 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$
K_2 (T)	$1.1 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	$7.5 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	$3.2 \cdot 10^{-3}$	$8 \cdot 10^{-3}$
n_1	2.1	3.2	2.1	3.2	2.1	3.1
n_2	1.7	2.7	1.7	2.7	1.7	2.7
w_1	0.94	0.75	0.65	0.74	0.63	0.78

Table 3. Neat PEEK and reinforced PEEK (150ca30), kinetic model parameters for three temperatures

For neat PEEK, the weight factor w_1 decreases from 0.94 to 0.63 when temperature increases from 300°C to 310°C. This evolution indicates that the main crystallization process has a strong contribution on total crystallization and also that the contribution of secondary crystallization mechanism is more important at high temperature. On the contrary for reinforced PEEK, the w_1 factor seems to be constant and there is always a strong contribution of the second mechanism.

The kinetic parameters K_1 and K_2 are largely influenced by temperature and presence of carbon fibres. K_1 and K_2 decrease when temperature increases. The identified kinetic parameters for reinforced PEEK are higher than those obtained for neat PEEK, that confirms the shorter crystallization time of reinforced PEEK. Correlation between experiment and model is always very good and is illustrated on Figure 5 for a temperature of 310°C. The contribution of the two crystallisation mechanisms as predicted with the model is also reported on the figure and gives confirmation that even if primary crystallisation starts first, the second mechanism has a contribution higher than 20% to the total crystallized mass fraction at this temperature.

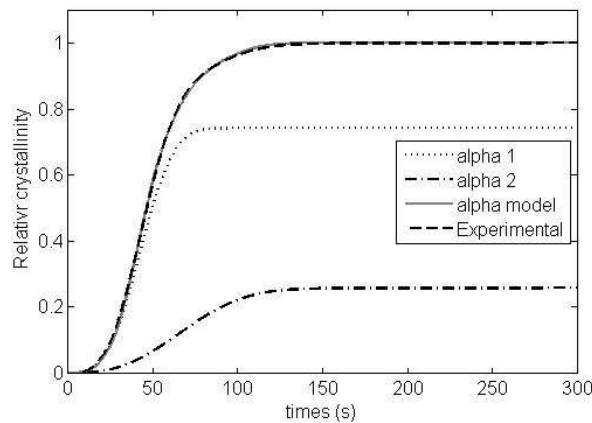


Figure 5. Reinforced PEEK Isothermal crystallization kinetic modelling at 305°C

4 Conclusion

Isothermal DSC measurements for neat and reinforced PEEK show that the introduction of fibers leads to modification of crystallization kinetics. With 30% of carbon fibers, the crystallization duration is less than for the neat matrix. In both cases, isothermal crystallization induces the occurrence of a second melting peak that characterizes two parallel crystallization mechanisms.

The use of a differential form of Avrami equation and considering that PEEK crystallization is induced by two complementary mechanisms, allows to model with a good accuracy isothermal crystallization. The identification of kinetics parameters for neat PEEK and

reinforced PEEK reveals the influence of fibers on crystallization kinetics. K_1 and K_2 kinetic parameters are more important for reinforced PEEK in accordance with experimental results. The values of Avrami exponents depend also on the material. So the n_1 were respectively 2.1 and 3.2 for neat and reinforced PEEK, suggesting an heterogeneous nucleation with three dimensional growth due to presence of fibers. The n_2 values in the latter stage (and related to mechanism two) of crystallization are 1.7 and 2.7 and are representative of an interface controlled growth.

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