

# MECHANICAL PERFORMANCES OF PEKK COMPOSITE MATERIALS LINKED TO THE PROCESSING PARAMETERS

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## ABSTRACT

Isothermal crystallizations of a poly(etherketoneketone) (PEKK) copolymer matrix prepared from diphenyl ether (DPE), terephthalic acid (T) and isophthalic acid (I) has been investigated by differential scanning calorimetry. Crystallization kinetics have been modeled by using a two stage modified Avrami model which takes into the complex crystallization of PEKK matrix. The influence of carbon fibers on PEKK crystallization kinetics has also been investigated for PEKK prepreg tapes. Based on those modelling, Time-Temperature-Transformation (TTT) diagrams of the crystallization of both neat resin and prepreps have been established providing an indispensable tool for PEKK composite processing. Finally, mechanical properties of neat PEKK resin samples having undergone different heat treatments have been measured to draw conclusions as the influence of crystallinity on final mechanical performances.

## 1. INTRODUCTION

High performance thermoplastic PAEK matrices are currently studied with a great deal in the aeronautic industry as matrix for the manufacturing of structural composite parts. In fact, PAEK composites have high temperature performances, good impact properties, high chemical and oxidation resistance and they are recyclable and weldable. They also can be consolidated out of autoclave and they are especially suitable for automated fiber placement. Those two last features would help to increase the aircraft production rate which is currently a major issue for aircraft manufacturers. The cockpit floor of the Airbus Defense and Space A400M aircraft manufactured out of autoclave with PEEK composite is an example. However, the main drawback of PEEK matrix is its high processing temperature (around 400°C) leading to high processing times and costs and potential degradation of the matrix during processing. PEKK which also belongs to PAEK family is nowadays much studied in the aircraft industry to compete with PEEK as matrix for composite structural parts. Indeed, for equivalent mechanical performances, PEKK matrix has a lower processing temperature (around 360°C) which simplifies its processing.

The final performances of composite parts are closely linked to their processing. For thermoplastic composites, the matrix crystallizes with different crystallinities and crystalline morphologies

depending on the processing thermal cycle which directly impacts the mechanical performances [1–4]. This is why, crystallization must be understood and controlled to be able to predict and thus optimize the mechanical performances depending on the processing thermal cycle.

The crystallization of PEKK has been studied by different authors since 90's [4–7]. It has been shown that PEKK crystallizes with a spherulitic radial growth and an instantaneous nucleation. It crystallizes with two distinct crystallization processes as it is the case of other thermoplastic polymers [8–13]. A first one, the primary crystallization which begins at the early stage of the crystallization and a second one, the secondary crystallization which would be attributed to the enhancement of the crystalline structure with the growth of a second crystalline structure within lamellae [5]. This subsidiary crystallization makes the crystallization kinetics modeling more difficult. Different isothermal crystallization models have been developed to incorporate the secondary crystallization, the most relevant reported are the Velisaris Seferis [14] and the Hillier [15] models. The Hillier model seems physically the most appropriated since it takes into account that the secondary crystallization can only grow from the primary crystallization whereas the Velisaris Seferis model postulates that both crystallization grow independently which is not consistent with previously explanations. However, the Hillier model is reduced to a 1D growth for the secondary crystallization. In a previous article [7], we have extended the Hillier model to describe any secondary crystallization mechanism. In this model, the relative volume fraction crystallinity  $\alpha(t)$  as a function of time is expressed by:

$$\alpha(t) = w_1 \left[ 1 - \exp(-K_1 t^{n_1}) \right] + w_2 K_2 n_2 \int_0^t \left[ 1 - \exp(-K_1 \theta^{n_1}) \right] (t - \theta)^{n_2 - 1} \exp[-K_2 (t - \theta)^{n_2}] d\theta \quad (1)$$

where  $w_1$  and  $w_2$  correspond to the weight factors between primary and secondary crystallizations ( $w_1 + w_2 = 1$ ),  $K_1$  and  $K_2$  to the crystallization rate constants and  $n_1$  and  $n_2$  to the Avrami exponents for the primary and the secondary crystallization respectively.

In this article, the modelling of the crystallization kinetics of neat PEKK and reinforced with carbon fibers with the modified Hillier model and the impact of crystallinity on the mechanical properties will be investigated to determine optimal thermal cycles for PEKK composite parts manufacturing.

## 2. EXPERIMENTAL

### 2.1 Material and preparation

PEKK matrices used in this study are provided by Arkema company. They are prepared from diphenyl ether (DPE), terephthalic acid (T) with para phenyl links and isophthalic acid (I) with meta phenyl links. Three different PEKK copolymer matrices have been studied referenced as PEKK 8002, 7002 and 6002 with T/I ratios of 80/20, 70/30 and 60/40 respectively. Their glass transition temperatures ( $T_g$ ) are around 155°C and their melting temperatures ( $T_m$ ) are around 360°C, 330°C and 300°C for PEKK 8002, 7002 and 6002 respectively. PEKK composites studied are tape prepregs reinforced with 60% carbon fiber volume.

### 2.2 Differential Scanning Calorimetry

Isothermal crystallization analyses were carried out in a TA Instruments Q2000 on granules of about 8 mg for the neat resin and on disk staking cut from tape prepregs with a total weight of about 21 mg. Specimens were first melted at 360°C during 5 minutes to erase the thermal history of the matrix, cooled at 60°C.min<sup>-1</sup> to the crystallization temperature and maintained during 3 hours. This cooling rate is high enough to ensure that the polymer does not crystallize before the isothermal crystallization. After crystallization, specimens were cooled to the room temperature and finally heated at 10°C.min<sup>-1</sup> to 360°C to measure the melting enthalpy.

## 2.3 Mechanical tests

Mechanical tests were carried out with an extensometric tensile test machine Instron 5966 equipped with an oven to make tests at high temperature. Tests were done on normalized 1BA tensile samples (ISO 527) with length of 75 mm, width of 5 mm for the fitting length and a thickness of 2 mm machined from amorphous plates of 100x100 mm<sup>2</sup> crystallized from the glassy state at 230°C for different times. Specimens were tested at room temperature and 180°C (above  $T_g$ ) with testing speed of 1 mm.min<sup>-1</sup> and 100 mm.min<sup>-1</sup> respectively. At 180°C, PEKK matrices are at the rubbery state and the testing speed must be high enough to measure entanglements network properties and not chain flow due to disentanglement.

## 3. RESULTS AND DISCUSSION

### 3.1. Isothermal crystallization kinetics modeling

Isothermal crystallizations have been carried out by DSC at different temperatures and for each of them, the evolution of the relative volume fraction crystallinity  $\alpha(t)$  has been calculated from the exothermic crystallization peak by:

$$\alpha(t) = \frac{\int_0^t Q(t) dt}{\int_0^{t_\infty} Q(t) dt} \quad (2)$$

where  $Q(t)$  is the heat flow measured at time  $t$  and  $t_\infty$  is the time when the polymer is fully crystallized. The parameters of the modified Hillier model presented previously (Equation (1)) have been then identified from the fitting of the model with the relative volume fraction crystallinity  $\alpha(t)$  calculated from DSC measurements (Equation (2)) for neat resin and charged with carbon fibers (Figure 1 and Figure 2). The Avrami exponent  $n_1$  has been set to 3 which corresponds to an instantaneous spherulitic growth according to the microscopic observations of PEKK crystallization [7] and  $n_2$  to 1 which corresponds to an instantaneous one dimensional growth and allowed the best fitting of the Hillier model with experiments. The evolution of the crystallization rate constants  $K_1$  and  $K_2$  as a function of temperature have been modeled with a Hoffman and Lauritzen model [16–18] which takes into account the nucleation and crystalline growth expressed by:

$$K_i(T) = K_{0i} \exp\left(-\frac{n_i U^*}{R(T - T_\infty)}\right) \exp\left(-\frac{n_i K_{gi}}{T \Delta T f}\right) \quad (3)$$

where  $K_{0i}$  is a pre-exponential factor independent of the 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,  $T_\infty$  is the temperature below which diffusion stops ( $T_\infty = T_g - 30K$ ) and  $R$  is the gas constant. The second exponential term is the contribution of the nucleation process, where  $K_{gi}$  is the activation energy of nucleation for a crystal with a critical size,  $\Delta T$  is the degree of supercooling ( $\Delta T = T_{m0} - T$ ) with  $T_{m0} = 340K$  [5] and  $f$  is a correction coefficient for the temperature dependence of the melting enthalpy ( $f = 2T / (T_{m0} + T)$ ). The index  $i$  is equal to 1 for primary crystallization and 2 for secondary crystallization with  $n_1 = 3$  and  $n_2 = 1$ .

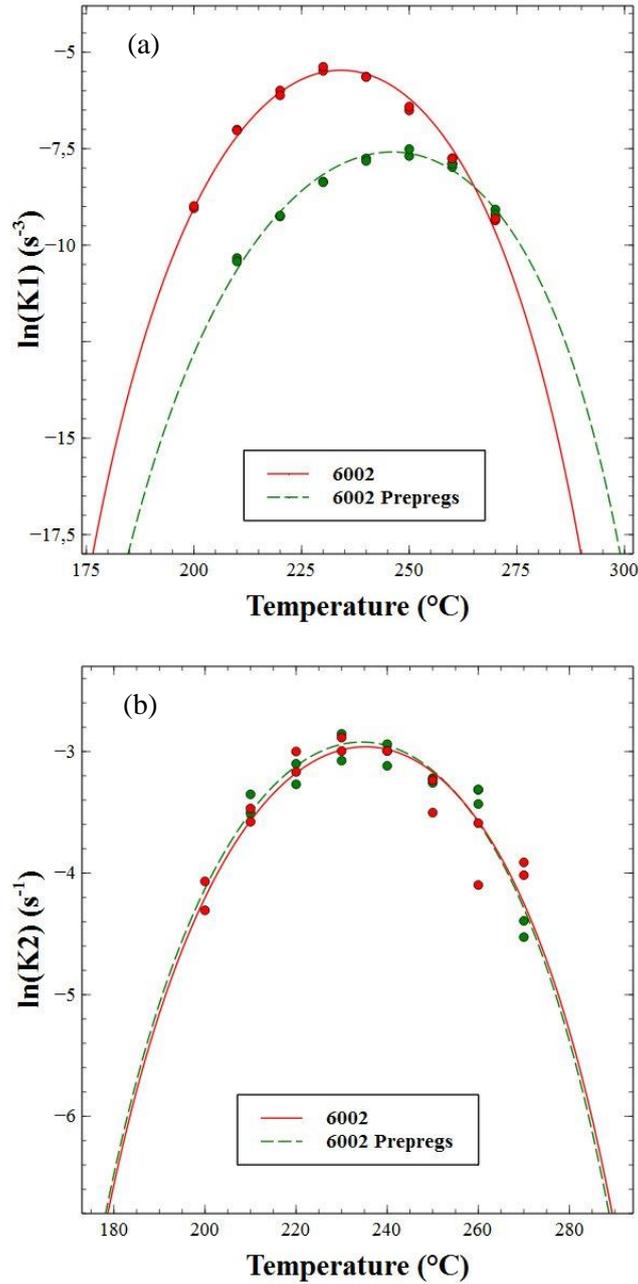


Figure 1: Logarithmic plots of the primary (a) and secondary crystallization (b) rate constants vs temperature for neat PEKK 6002 (solid line) and charged with carbon fibers (dashed line) with the Hoffman and Lauritzen model fitting

In Figure 1, we observed that the evolution of the crystallization rate constants as a function of temperature have typical bell shapes which is consistent with the Hoffman and Lauritzen theory (Equation (3)). For the primary crystallization (Figure 1 a), the crystallization rate reaches a peak at around 230°C for the neat resin and 250°C with carbon fibers. It can also be noticed that crystallization rates for PEKK prepregs are higher than the neat resin at crystallization temperatures above 270°C which is the opposite for lower crystallization temperatures. This phenomenon could be explained by the fact that carbon fibers play the role of nucleating agents especially at high temperature where the homogeneous nucleation from the bulk is very slow. For lower temperatures, the homogeneous nucleation increases and thus carbon fibers have less effect on nucleation and they could hinder the macromolecular chain mobility which could explains the lower crystallization rate of the matrix charged with carbon fibers compared to the neat resin below 270°C.

For the secondary crystallization (Figure 1 b), carbon fibers do not seem to influence the crystallization rate since the curves for the prepregs and the neat resin are quite the same. For both, the maximum crystallization rate is reached around 240°C.

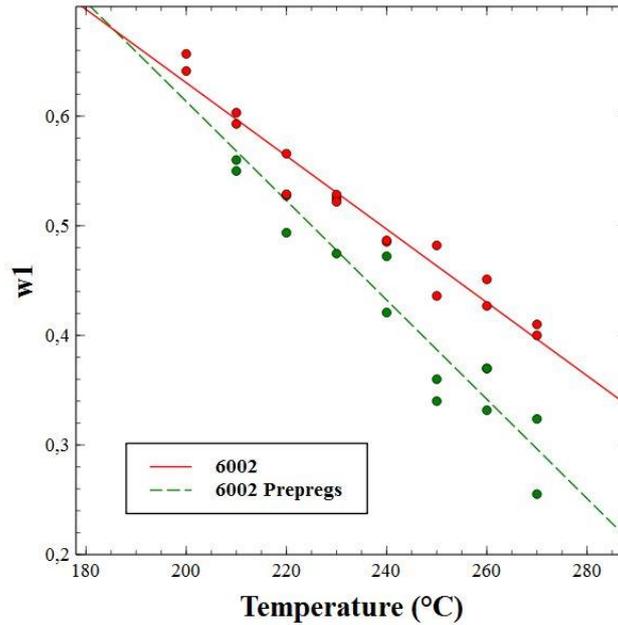


Figure 2: Weight factor of the primary (a) and secondary crystallization (b) vs temperature for neat PEKK 6002 (solid line) and charged with carbon fibers (dashed line) with the linear model fitting

The weight factor for the primary crystallization  $w_1$  (Figure 2) has been modeled with a linear equation expressed by:

$$w_1(T) = a_1T + b_1 \quad (4)$$

where  $a_1$  and  $b_1$  are two constants independent of the temperature. We observed that  $w_1$  decreases with the crystallization temperature showing that the formation of the secondary crystallization is promoted for low degree of supercooling. This observation has also been reported by few authors [4,7,19] with the increase with the annealing temperature of the area of an 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 the chains allowing the enhancement of the crystalline phase. Secondly, we observed that crystallization weight factor for the prepregs is lower than for the neat resin which could be attributed to the fact that there are more blocked chains in the amorphous phase due to carbon fibers which can reorganized and form secondary crystallization.

### 3.2. Time Temperature Transition (TTT) diagrams

From the identification of the Hillier parameters ( $K_1$ ,  $K_2$  and  $w_1$ ) and their modeling as a function of temperature, the evolution of the crystallinity depending of the crystallization temperature and time has been plotted in Time-Temperature-Transformation (TTT) diagrams for the neat PEKK resin and charged with carbon fibers (Figure 2). TTT diagrams are very useful for composite processing since they allow to predict the crystallinity depending on thermal processing cycles. We observed that despite different crystallization mechanisms and crystallization kinetics for the primary and the secondary crystallization, TTT diagrams of the neat resin and the prepregs are similar. This is

consistent with the article of Hsia et al. [6] on composite PEKK crystallization which concluded that carbon fibers have a only a small effect on the matrix crystallization kinetics.

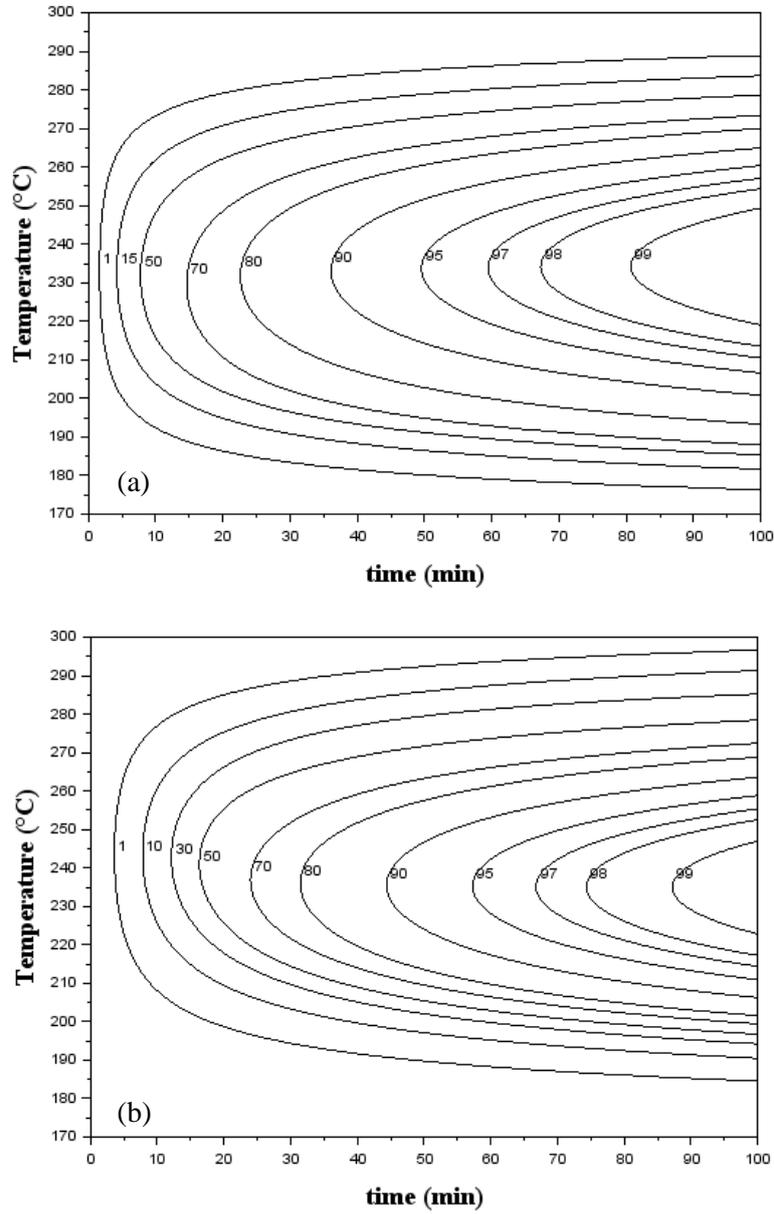


Figure 3: TTT diagrams of the relative volume fraction crystallinity for neat PEKK 6002 (a) and charged with carbon fibers (b)

### 3.3. Influence of the crystallinity on the mechanical properties

#### 3.3.1 Tests at room temperature

The evolution of the Young modulus and the strain at break as a function of crystallinity for PEKK 8002, 7002 and 6002 neat resins tested at room temperature has been plotted in Figure 4. We observed an increase of the Young modulus with crystallinity which is the opposite for the strain at break. The Young modulus increases by 1GPa for fully crystallized PEKK. It can be noticed that PEKK 7002 and 8002 have higher Young modulus than PEKK 6002 because they crystallize more. For the strain at break, we observed a drop of the properties of about 150% between the amorphous and the fully crystallized matrices. It can be concluded that crystallinity makes the matrix tougher but also more brittle.

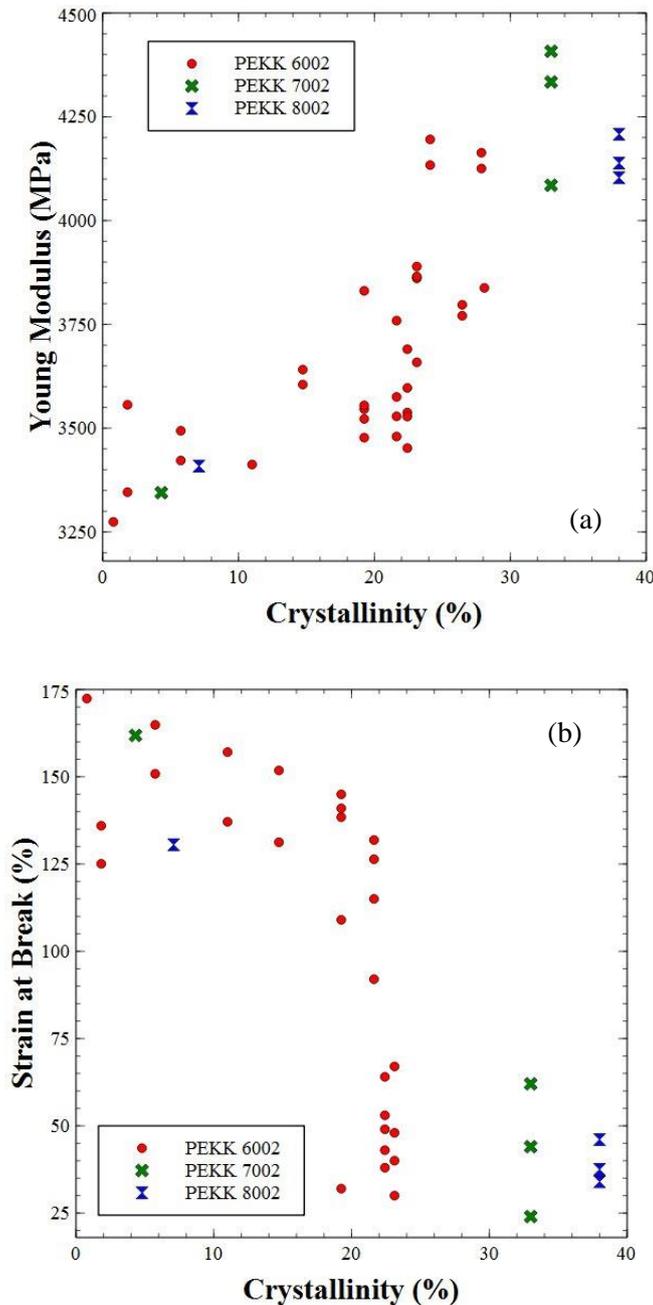


Figure 4: Young modulus (a) and strain at break (b) vs crystallinity for PEKK 6002, 7002 and 8002 tested at room temperature

### 3.3.2 Tests at 180°C

For tests at 180°C, only the Young modulus could be measured. In fact, for this temperature the matrix are at the rubbery state and thus strain at breaks are too high to be measured with the tensile test machine. As expected, we first observed a drop of the Young modulus compared to the room temperature tests and an increase of the Young modulus with crystallinity which is more important than for the room temperature tests. In fact, for the matrix barely crystallized the Young modulus is around 5 MPa and it rises until 200 MPa for PEKK 6002, 600 MPa for PEKK 7002 and 1600 MPa for PEKK 8002. This gap between matrices is due to their maximal crystallinity which is about 28%, 34% and 38% respectively. It can be thus concluded that the crystalline phase has a strong impact on the mechanical properties especially above the glass transition temperature.

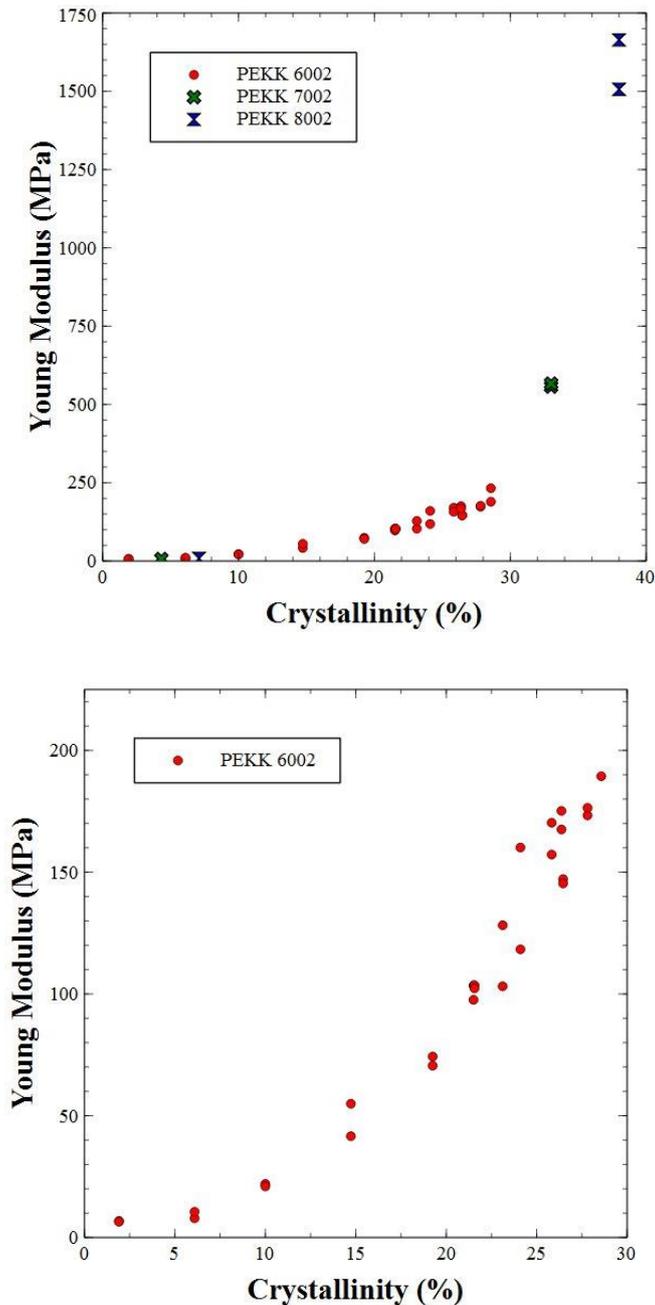


Figure 5: Young modulus vs crystallinity for PEKK 6002, 7002 and 8002 tested at 180°C

#### 4. CONCLUSION

The main results of this article have been to develop a complete method for PEKK composite crystallization modeling as well as build their TTT diagrams which are necessary tools for their processing. Furthermore, this method is applicable for any thermoplastic composite. We showed that the presence of carbon fibers has a small effect on the matrix crystallization kinetics despite different crystallization mechanisms. It has been established that the mechanical properties have a strong link with crystallinity especially above the glass transition temperature. In fact, the Young modulus increases with crystallinity which is the opposite for the strain at break. Further mechanical tests will be carried out on PEKK composites.

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