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# DSC INVESTIGATION OF THE INFLUENCE OF CARBON CONTENT ON PEEK CRYSTALLISATION AND STABILITY

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## 1 Introduction

Properties of semi-crystalline thermoplastics are known to be heavily dependent on the degree of crystallinity and therefore on the cooling conditions. This influence of cooling rate on properties has been observed in structural thermoplastic composites, but the influence of carbon fibers on the crystallisation behavior remains poorly known. Indeed, apart from the role of carbon fibers on nucleation that has already been related in literature, its influence on the entire crystallization process is still poorly understood [1].

Among the semi-crystalline thermoplastics used as composite matrix, PEEK is of major interest due to its high glass transition temperature and mechanical performances. Therefore, assessing the influence of carbon fibers on PEEK crystallization is required in prospect of composite performance optimization.

Neat PEEK exhibits an unusual crystallisation behavior resulting in the apparition of two distinct melting peaks on endothermic thermograms [2-4]. The origin of this secondary melting peak is still discussed but recent studies tend to show that it would refer to an imperfect crystal structure and/or a low thickness lamellar structure [2,5,6]. This phase is however always taken into account when measuring the degree of crystallinity thanks to Differential Scanning Calorimetry (DSC) traces.

The aim of this study is therefore to assess the influence of "long" carbon fibers on PEEK crystallisation [7]. The crystallisation kinetics, heat of fusion and DSC scans are analyzed and the influence of carbon content on neat PEEK stability and crystallisation behavior is discussed.

## 2 Materials

Polymer used in this study is a Poly-Ether-Ether-Ketone (PEEK) provided as coarse powder by Victrex (grade 150). This polymer is a common grade used as matrix in structural composites. Carbon fibers are HR fibers removed from a quadriaxial Non-Crimp Fabric (NCF). The removed carbon yarns have been cut in order to obtain 5mm long carbon fibers.

## 2 Experimental procedures

Aluminum sealed pans have been prepared with 3 to 5mg of PEEK powder and different carbon fiber contents. By controlling the carbon weight ratio, DSC samples of "C/PEEK composites" were thus obtained with 18 to 72%wt of carbon fibers. It is actually assumed in this study that this annealing stage favors the blend homogenization and that the material in the DSC pans can be considered as representative composite materials.

DSC measurements have been performed with a Perkin Elmer DSC 8000 apparatus. All the tests have been started by applying a 5min isothermal annealing stage at 400°C so as to perform crystallisation from a nuclei-free melt.

From this molten state, two different cooling conditions have been achieved. Isothermal crystallisation have been realized at 305°C or 310°C during 15min. A constant cooling ramp of 150°C.min$^{-1}$ was used to cool the samples from melt before and after the isothermal step. Non-isothermal crystallisation has also been performed during 20°C.min$^{-1}$ cooling ramps. Whatever crystallisation condition used, the melting endotherms were measured during 10°C.min$^{-1}$ heating scans.

Many different results have been collected on the crystallisation exotherms and melting endotherms: crystallisation and melting temperatures, heat of fusion and degree of crystallinity, crystallisation kinetics. The transformation rate was assessed from the crystallization heat flux by using the partial area method, and the mass fraction crystallinity was determined from melting DSC traces in considering a reference enthalpy of fusion of 130 $J.g^{-1}$ [23].

## 3 Influence of carbon fibers ratio

Concerning non-isothermal crystallisation, Fig 1 shows the crystallisation kinetic for different carbon ratios when subjected to a cooling ramp of 20°$C.min^{-1}$. The curves exhibit a typical sigmoidal shape which point of inflection corresponds to the maximum crystallisation kinetic. No sudden change is discernible on the sigmoidal curves, which reveal occurrence of a continuous crystallization process whatever the carbon fiber content.

For all different materials, crystallisation occurs within 2.5 minutes, but crystallisation starts earlier for samples filled with carbon fibers, which confirms the nucleation effect of the fibers surface. This crystallization precocity is all the more true that the fiber content is high.

However, the half-time crystallization kinetic (i.e. the kinetic for a relative crystallinity of 0.5) does not seem to be dependent on the carbon fibers ratio. This constant maximum crystallisation kinetic suggests that the development of the crystalline structure is not affected by the carbon fibers, except for the nucleation phase.

As already reported in the literature, PEEK has a particular crystallisation behavior characterized by the apparition of a secondary melting peak on the DSC traces. This secondary melting peak appears when samples are crystallized at low cooling rates (<10°$C.min^{-1}$) or when samples are isothermally crystallized.

Fig. 2 and Fig. 3 show the melting DSC curves respectively resulting from isothermal (305°C) and non-isothermal crystallizations (-20°$C.min^{-1}$) for different carbon fiber ratios. The double melting peak is clearly observable in Fig 2 for neat PEEK and, as expected, only one peak is visible for samples of neat PEEK cooled at 20°$C.min^{-1}$ (Fig. 3). The DSC traces recorded for carbon fibers composites shows that fibers do not modify the conditions of appearance of a secondary melting peak. Whatever the carbon fiber content, isothermally cooled samples exhibit two melting peaks and samples cooled at 20°$C.min^{-1}$ only display one peak. Moreover, the temperature of the melting peaks remains constant with increasing the carbon fibers content.

The fact that carbon fibers do not modify both the maximum crystallization kinetics and melting temperatures but only the nucleation process suggest that the appearance of a double melting peak only depends on the crystal growth mechanisms.

Nevertheless, despite its nucleation ability, the presence of carbon fibers is not beneficial for total crystallinity. As plotted in Fig 4, the higher the carbon fiber content is, the lower is the PEEK degree of crystallinity. As a consequence, according to the literature, increasing the fiber content in composite structural parts may lead to a drop of the matrix properties. However, the decrease of the degree of crystallinity is less than 7 points and the loss in matrix properties may be sensible.

## 4 Influence of ageing on crystallization

Carbon/PEEK composites are commonly processed by autoclave or in a hot press that are rough processes for high temperature polymer matrices. Indeed, during the processing cycle, impregnation of carbon fibers requires to maintain PEEK matrix at high temperature and pressure during several tens of minutes. Due to the organic nature of PEEK polymer, degradation may occur and must be taken into account when optimizing processing conditions.

In order to evaluate the influence of ageing on the crystallisation behavior of PEEK and Carbon/PEEK composites, heating and cooling cycles have thus been achieved to samples with various carbon fiber ratios.

First, DSC samples with 47 and 59%wt of carbon fibers have been heated up and maintained during 2h at 400°C. After this ageing period, the samples have been isothermally crystallized at 310°C for 15 min using the method previously described. The crystallization kinetic has then been determined from the curves by applying the partial area method.

As shown in Fig. 5, ageing of Carbon/PEEK samples results in a variation of the crystallization behavior that show evidence of degradation. Indeed, after ageing, the sigmoidal shape is modified, and in particular crystallization duration increase with ageing and with the carbon fiber content. Moreover, ageing results in a noticeable decrease of the maximum crystallisation kinetic (slope at the inflection point) but also on a decrease of the transformed fraction at maximum crystallization kinetic.

Secondly, in order to characterize the evolution of degradation effects, short ageing cycles have been achieved to samples with various carbon fibers ratios. One cycle consisted in a 5 minutes long isothermal step at 400°C followed by a cooling phase at 20°C.min$^{-1}$ and by a heating phase at 10°C.min$^{-1}$. The melting temperature and degree of crystallinity have been systematically determined during the melting phase. Fig. 6 shows the evolution of the melting temperature and degree of crystallinity with cycles for neat PEEK and Carbon/PEEK. Neat PEEK exhibits a quite good stability after 20 ageing cycles. Its melting temperature and degree of crystallinity remains almost constant although the curves show a progressive decreasing trend through cycling. In opposition, ageing cycles induce a significant decrease of the melting temperature and degree of crystallinity in carbon/PEEK composites. It can also be noticed that, despite the fluctuations due to measurement accuracy, the effects of degradation are gradual with a linear decrease of the physical properties. This influence is particularly marked for composites with high fiber ratios. Indeed, after only 8 cycles, i.e. for a total isotherm duration of 40min, the composite with 72%wt of carbon exhibits a decrease of 3,5°C of the melting temperature and of 2,5 points of the mass degree of crystallinity.

These evolutions with ageing can be explained by the results of Day et al. Indeed, they showed that PEEK degradation is the consequence of crosslinking development between polymer chains and that air environment may increase the degradation rate [8,9]. The increase of chains entanglement due to crosslinking may then make chains folding and arrangement more complex during crystallization, which consequence would be lower melting temperature and degree of crystallinity.

Thermal ageing has low influence on neat PEEK but such a rapid degradation is surprising in PEEK composites since it occurs in a neutral environment (DSC oven). Therefore it can be assumed that the carbon surface is responsible of degradation initiation and that the degradation rate is all the more rapid that the carbon fiber content is high. The sizing on carbon fiber surface that contains oxygen atoms may be responsible of this degradation process.

**Conclusions**

Performing DSC scans on PEEK matrix filled with controlled carbon fiber ratios has allowed to characterize PEEK crystallization behavior with accuracy. The results show that carbons fibers, apart from crystallization initiation and nucleation that decrease crystallization duration, do not modify the global crystallization process. In particular, the sigmoidal shape of crystallization kinetics remains constant as well as the maximum kinetic at inflection point. Surprisingly, carbon fibers however induce a lower degree of crystallinity, variation that cannot be explained by the unique change in nucleation.

Moreover, if the presence of carbon fibers has limited effect on PEEK crystallization, it strongly influences PEEK stability. Indeed, after a few minutes at high temperature, it has been observed that PEEK matrix exhibits lower melting temperature and crystallinity that can be related to crosslinking development between the polymer chains.

Finally, this study shows that particular attention must be paid to the matrix evolution when processing Carbon/PEEK composites at high temperature. Indeed, the effects of carbon fibers on PEEK stability may have been minimized due to the neutral environment in DSC. Larger degradation effects can thus be expected in air environment.

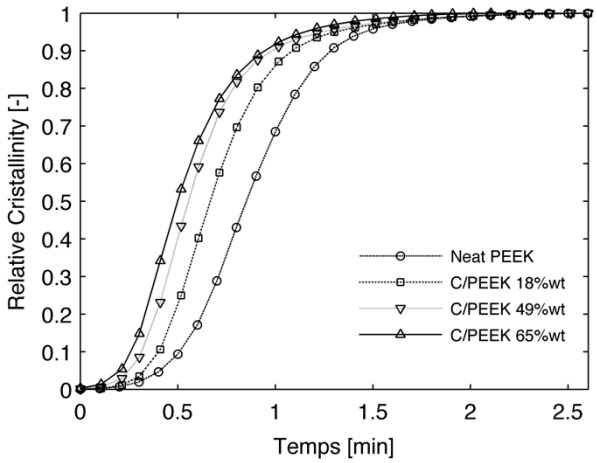


Fig.1. Influence of carbon fiber content on non-isothermal crystallisation kinetic (20°C.min$^{-1}$ cooling)

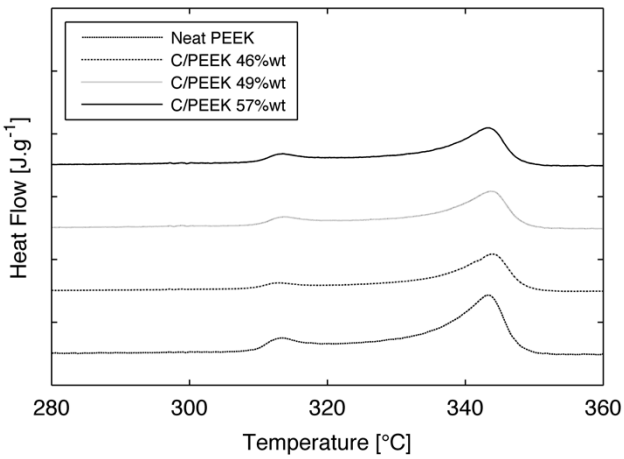


Fig. 2. Melting DSC traces resulting from isothermal crystallisation at 305°C

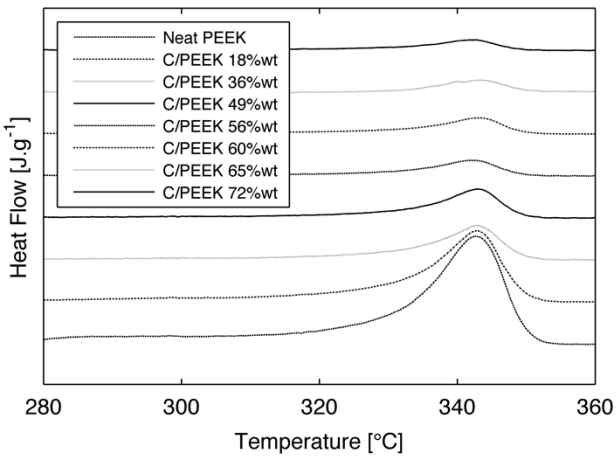


Fig. 3. Melting thermograms resulting from non-isothermal crystallisation at 20°C.min$^{-1}$

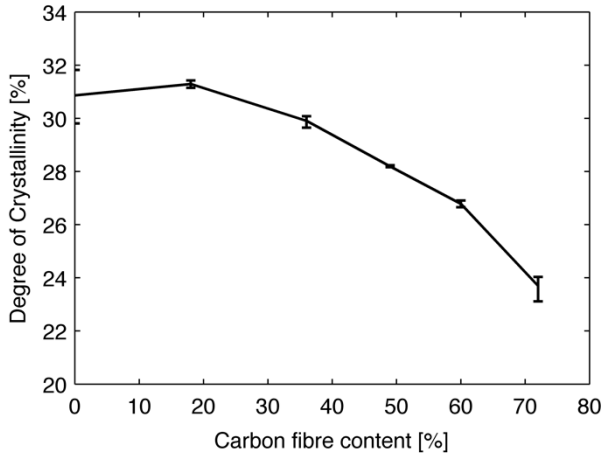


Fig. 4. Influence of carbon fiber ratio on PEEK total degree of crystallinity (non-isothermal crystallisation at 20°C.min$^{-1}$)

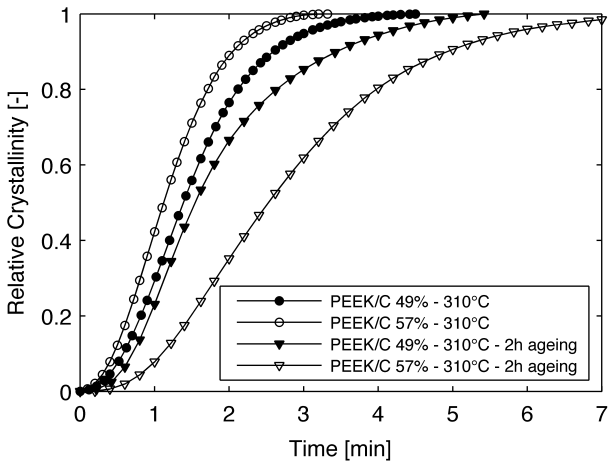


Fig. 5. Influence of ageing at 400°C on crystallization kinetic of Carbon/PEEK composites

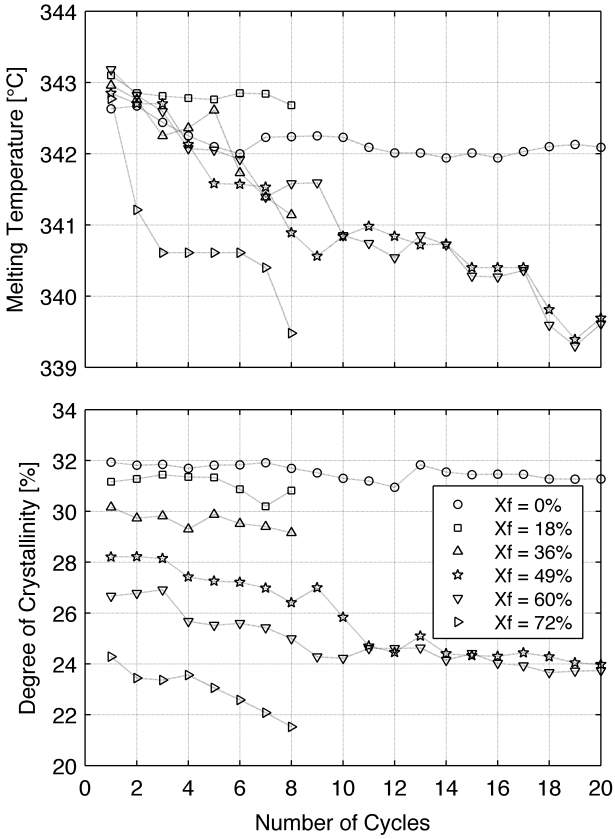


Fig. 6. Variation of melting temperature and degree of crystallinity with ageing cycles at 400°C

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