



## Opposite role of different carbon fiber reinforcements on the non-isothermal crystallization behavior of poly(etheretherketone)



Marco Regis <sup>a, b</sup>, Marco Zanetti <sup>a</sup>, Michele Pressacco <sup>b</sup>, Pierangiola Bracco <sup>a, \*</sup>

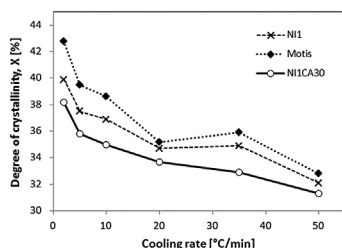
<sup>a</sup> Department of Chemistry and NIS (Nanostructured Interfaces and Surfaces) Centre, University of Turin, Turin, Italy

<sup>b</sup> R&D Department, Limacorporate SpA, Villanova di S. Daniele, UD, Italy

### HIGHLIGHTS

- A non isothermal crystallization study for PEEK and two CFR PEEK is proposed.
- Fibers influence the polymer crystallization by either favoring or hindering it.
- Fibers and processing conditions must be considered for optimal polymer morphology.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 5 February 2016

Received in revised form

9 May 2016

Accepted 12 May 2016

Available online 19 May 2016

#### Keywords:

Composite materials

Polymers

Crystallization

Differential scanning calorimetry (DSC)

### ABSTRACT

A non-isothermal crystallization study on two different 30%w carbon fiber (PAN and pitch-based) reinforced PEEK was performed by differential scanning calorimetry (DSC), aiming to provide more information on PEEK crystallization behavior in the presence of reinforcements. Melt crystallization was performed by cooling down the CFR-PEEK samples from the molten state with different cooling rates (from 2 to 50 °C/min). Samples were subsequently heated up again at 400 °C at 20 °C/min to evaluate any potential differentiation in the created crystal structures. The same experiments were run also for unfilled PEEK, taken as reference. Crystallization kinetics (with Avrami and Avrami-Ozawa approaches), and activation energies (according to Friedman method) were evaluated. The results showed that the cooling rate influences crystal growth and morphology but also, more importantly, that fiber type affects the crystallization mechanisms, either favoring or hindering polymer crystallization, depending on the fiber characteristics, geometry and density. Overall, these observations suggest that accurate fiber selection and processing conditions set up have to be chosen to ensure an optimal polymer morphology.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

In the last decades, poly(etheretherketone) (PEEK) has been shown to be one of the most promising structural polymers for a wide range of industrial sectors, such as aerospace, biomedical, and

high temperature applications, due to its high transition temperature and strong chemical resistance to various agents [1,2]. More recently, also PEEK composites have been looked at as promising materials, thanks to their enhanced mechanical properties and strength to weight ratio [3].

As for every semi-crystalline polymer, PEEK properties largely depend upon molecular weight and crystallinity. Due to its high melting temperature, the processing conditions are often highly demanding, implying high temperatures (up to 400 °C) and sensitive cooling steps, which affect the polymer morphology. For this

\* Corresponding author. Department of Chemistry and NIS Center, University of Turin, Via Pietro Giuria, 7, 10125 Torino, Italy.

E-mail address: [pierangiola.bracco@unito.it](mailto:pierangiola.bracco@unito.it) (P. Bracco).

reason, a considerable amount of research has been carried out to determine the influence of the thermal history on PEEK crystallinity and crystallization behavior, often with controversial results [4–7]. Unvocally, it was found that PEEK exhibits a double melting peak, despite different interpretations have been given for such behavior [8–10]. Nowadays, the most acknowledged theory is based on a combination of the simultaneous partial melting and recrystallization of the polymer crystal domains [7,11]. Several studies, based on different techniques (i.e. DSC, WAXS/SAXS, FT-IR, etc.) supported this indication [6,12,13].

When studying PEEK crystallization behavior, both isothermal and non-isothermal approaches have been used [5,11,14,15]. Kinetic aspects of the crystallization process were usually described by the Avrami theory or alternative methods [14,16,17], but studies performed so far are often discordant and most models were proven to be inadequate to some extent, especially when considering the addition of reinforcements [3,7,18,19], to the point that no clear indication on the effect of the reinforcement on the crystallization behavior of the polymer can be obtained.

Therefore, providing more data on PEEK composites crystallization behavior, as a function of the reinforcement typology and characteristics, is still needed to understand the crystallization mechanism of the final composite material.

The present work investigates PEEK crystallization in the presence of two different carbon fiber reinforcements (CFR). The use of a non-isothermal approach has been preferred, since PEEK and PEEK composites processing (i.e. extrusion or compression molding) is usually performed under dynamic non-isothermal conditions. It is therefore of interest to provide information on the effect of thermal history on the crystalline structure of the considered materials, in the presence of fibers with different characteristics. The results obtained on the composites were compared with those of non-reinforced PEEK, in order to assess any deviation from the crystallization of the neat polymer.

## 2. Materials and methods

The materials of choice for the study were an unfilled biomedical grade PEEK (NI1) and two formulations of biomedical grade 30% wt. carbon fiber reinforced (CFR) PEEK, PAN and pitch based, named NI1CA30 and Motis, respectively (Invibio, UK). Only 30% wt. formulations are available for biomedical applications, therefore different reinforcement percentages were not considered. The carbon fibers have different mechanical properties, dimensions, and densities: Young's modulus and fiber diameter are 540 GPa and  $6 \pm 2 \mu\text{m}$  for PAN carbon fibers, and 280 GPa and  $10 \pm 2 \mu\text{m}$  for pitch carbon fibers, respectively, while density is  $1.76 \text{ g/cm}^3$  and  $2 \text{ g/cm}^3$  for PAN and pitch carbon fibers, respectively [20].

Melt crystallization DSC studies were carried out to assess the crystallization behavior of the selected materials. As mentioned in the introduction, non-isothermal melt crystallization was chosen in spite of a more conventional isothermal approach to better simulate the processing conditions of PEEK and CFR-PEEK. Cold crystallization has not been considered since the transformation process implies a cooling step from the molten state, rather than heating steps from the glassy state.

The non-isothermal melt crystallization studies were carried out in a TA Q20 DSC (TA inc, USA). 6.5–8.5 mg samples were encapsulated in hermetic pans. The first DSC step was a preliminary heating up stage at  $400 \text{ }^\circ\text{C}$  for 15 min, to erase previous thermal history and ensure a nuclei-free melt. This procedure is generally applied in non-isothermal studies, since it allows to erase the previous thermal effects on the polymer, i.e. crystallization during processing conditions, and ensures that crystallization behavior observed during the study is not significantly influenced by the

sample preparation procedure [3,21]. After the heating step, samples were cooled down to  $30 \text{ }^\circ\text{C}$  at different cooling rates (2, 5, 10, 20 and  $50 \text{ }^\circ\text{C/min}$ ). Although thermal lag is known to affect the accuracy of the DSC results [22], a number of studies have demonstrated that it has a moderate effect within the range of cooling rates and sample masses investigated here [9,22]. The selected cooling rates are considered to be representative of a standard injection molding process. Typically, injection molded material is kept at a temperature above the  $T_m$  (usually  $400 \text{ }^\circ\text{C}$  or slightly less) as it flows inside the mold, which is kept at a lower temperature, e.g.  $250 \text{ }^\circ\text{C}$ . Polymer flow and holding time usually takes 2–3 min, depending upon the complexity of the part to be realized, then the molds are opened and the molded polymer shape is naturally cooled in air, where it reaches RT within 5 min. With these processing steps, it is believed that the overall cooling rate of the material should range from around  $30\text{--}50 \text{ }^\circ\text{C/min}$  to  $100\text{--}150 \text{ }^\circ\text{C/min}$ , which partly overlaps the selected cooling rates. All tests were run in triplicate. The DSC apparatus was calibrated with indium and zinc for each of the cooling rates used in this study.

After the crystallization study, the resulting samples were subjected to an additional heating run, up to  $400 \text{ }^\circ\text{C}$  at  $20 \text{ }^\circ\text{C/min}$ . Samples were then held at  $400 \text{ }^\circ\text{C}$  for 5 min and cooled down to  $30 \text{ }^\circ\text{C}$  at  $20 \text{ }^\circ\text{C/min}$ .

% Crystallinity was calculated as

$$X\% = \frac{\Delta H_f}{\Delta H_f^0 \cdot v_m} \cdot 100 \quad (1)$$

where  $\Delta H_f^0 = 130 \text{ J/g}$  is the theoretical heat of fusion of pure crystalline PEEK [4] and  $v_m$  is the polymer content.

## 3. Results and discussion

### 3.1. Non-isothermal crystallization behavior

The crystallization exotherms of pure, unreinforced PEEK and of both CFR PEEK formulations at different cooling rates are presented in Fig. 1.

The crystallization enthalpies (Table 1), calculated from the area under the DSC curve and corrected for the actual weight ratio of the polymer (70%) in the two CFR formulations, decrease as the cooling rate increases, as can be expected due to a shorter time allowed for crystallization, which will result in a lower total crystallinity. Only slight differences were observed among the three formulations: at low cooling rates ( $\leq 10 \text{ }^\circ\text{C/min}$ ), the crystallization enthalpy of NI1CA30 is constantly lower than that of NI1 and Motis.

The peak crystallization temperature ( $T_c$ ) of the unfilled material decreases as the cooling rate increases (Table 1 and Fig. 2), since crystallization time at higher cooling rates is lower.

The same behavior has been observed also for the two CFR formulations, although slightly higher and lower  $T_c$  have been found for Motis and NI1CA30 CFR-PEEK respectively, when compared to neat PEEK.

According to what reported in previous literature studies [3,18,19], there are two major mechanisms affecting the crystallization of PEEK composites: heterogeneous nucleation and mobility of chain segments. When comparing the behavior of a CFR PEEK to that of neat PEEK, if heterogeneous nucleation is dominating, crystallization will occur at lower supercooling (i.e.  $T_c$  will be shifted to higher values); conversely, if the presence of the filler results in predominating hindrance of mobility of chain segments,  $T_c$  will be shifted to lower values. Additionally, the filler was proposed to have an influence, under cooling rates slower than the

Download English Version:

<https://daneshyari.com/en/article/1520755>

Download Persian Version:

<https://daneshyari.com/article/1520755>

[Daneshyari.com](https://daneshyari.com)