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Isothermal crystallization kinetic modeling of poly(etherketoneketone) (PEKK) copolymer

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ABSTRACT

Isothermal melt and cold crystallizations of a poly(etherketoneketone) (PEKK) copolymer prepared from diphenyl ether (DPE), terephthalic acid (T) and isophthalic acid (I) with a T/I ratio of 60/40 have been investigated by differential scanning calorimetry, wide-angle X-ray scattering and polarized optical microscopy. For the first time, the two-stage overall crystallization kinetics of PEKK taking into account effects of nucleation and crystal growth has been identified by using a modified Hillier type model. The primary crystallization stage is found to be an instantaneous two dimensional nucleation growth with an Avrami exponent of 2 whereas the secondary stage is found to be an instantaneous one dimensional nucleation growth with an Avrami exponent of 1. The evolution of the crystallization kinetic constants for two-stage crystallizations has been modeled according to the Hoffman and Lauritzen growth theory. Due to low crystallization kinetics, a crystallization induction time has been added to obtain a good fit with experimental data. Based on this modeling, Time-Temperature-Transformation (TTT) diagrams of the relative volume crystallinity have been established for the overall crystallization mechanism and also for the separated primary and secondary crystallization mechanisms providing an original crystallization mapping of the material.

1. Introduction

High performance thermoplastic poly(aryletherketone) (PAEK) matrices are increasingly used in aeronautics for composite structural parts. They have high temperature performances, good impact properties, high chemical and oxidation resistance and as all thermoplastics, they are recyclable and weldable. They are especially suitable for automated composite fiber tape placement and for out of autoclave consolidation. Those two features would help increase the aircraft production rate which is currently a major issue for aircraft manufacturers.

PAEKs differ from each other in the ratio of ether/ketone. PEEK has been the most studied since the 1990s [1–8] because of its high temperature performances, and its chemical and oxidation resistance. However, it has a high melting temperature which makes its processing difficult. PEKK copolymers have been studied by few authors in the 1990s [9–14] and they have not aroused great interest until recently [15–18]. They are prepared form diphenyl ether (DPE), terephathlic acid (T) with para phenyl links and isophthalic acid (I) with meta phenyl links and differ from each other with their T/I ratios. Their melting temperatures (T_m) decrease with the T/I ratio without changing significantly their glass transition temperature (T_g) [9]. This is due to a lowering of the macromolecular chains regularity with the T/I ratio which decreases the crystalline phase compactness [9]. PEKK 60/40 has a T_g about 156 °C and a T_m about 300 °C [18], which is lower than the one for PEEK (around 340 °C [2]). This is quite interesting for processing regarding part manufacturing costs and possible degradation at high temperature. At last, PEKK 60/40 crystallizes less and slower than PEEK because ketone linkages are stiffer than ether linkages. The maximum crystallinity varies between 22% and 27% and it does not crystallize for cooling rates above 10 °C.min^{-1} [18].

Isothermal crystallization mechanisms of PEKK 60/40 have been studied by Gardner et al. [9] and Cortés et al. [18]. After annealing, they observed an additional endotherm during the melting which occurs about 10 °C above the annealing temperature. Such behavior has also been observed for PEEK [2,4,19] and other semi-crystalline polymers as poly(ethyleneterephthalate) [20–22] and is called the

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double-melting behavior. This additional endotherm is attributed to the melting of a secondary crystallization associated to the growth of an interlamellar crystalline structure within lamellae [23]. This subsidiary crystallization appears after long annealing or slow cooling rates. Gardner et al. [9] also studied the PEKK 60/40 isothermal crystallization kinetics with a peak-time method (time for which the crystallization exothermic peak is maximum) [9] but did not use a crystallization kinetic model taking into account the two-stage crystallization.

Different studies have been made to incorporate the two-stage crystallization into the crystallization kinetic modeling of polymers, the two most relevant reported are the Velisaris Seferis [5] and the Hillier models [23]. The former postulates that two Avrami type crystallization processes [24] occur in parallel independently whereas the second assumes that a primary Avrami type crystallization process occurs followed by a first order crystallization process which grows from the primary crystallization. Hsiao et al. [12] investigated the isothermal crystallization kinetics of a PEKK 70/30 with a modified Hillier model which postulates that the secondary crystallization is not necessarily a first order process and compared it to the Velisaris Seferis model. They concluded that the modified Hillier model has a better physical meaning than the Velisaris Seferis one because it is more suitable to describe the growth of a second crystalline structure within lamellae. In this model, the primary crystallization is expressed by an Avrami equation:

$$\alpha_1(t) = 1 - \exp(-K_1 t^{n_1}) \tag{1}$$

where α_1(t) is the relative volume fraction crystallinity at time t, w_1 is the weight factor between primary and secondary crystallizations, K_1 is the crystallization rate constant both depending on the annealing temperature and n_1 the Avrami exponent depending on the nucleation and the growth geometry, for the first mechanism. The secondary crystallization process which occurs once a volume element has been included in the lamellae at time θ is expressed by an Avrami equation:

$$\alpha_2(t) = \int_0^t \alpha_1(\theta) \times \frac{d}{dt}(\alpha_2(t-\theta))d\theta \tag{2}$$

where $\alpha_2(t\text{-}\theta)$ is the relative volume fraction crystallinity at time t, w2 is the weight factor, K_2 is the crystallization rate constant both depending on the annealing temperature and n_2 the Avrami exponent depending on the nucleation and the growth geometry, for the second mechanism. The Avrami exponent n_2 is not necessarily equal to 1 according to Hsiao et al. [12]. The total crystallinity at time t arising from those two consecutive crystallization processes becomes:

$$\alpha(t) = w_1\alpha_1(t) + w_2\alpha_2(t) \tag{3}$$

From Equations (1)–(3):

$$\alpha(t) = w_1[1 - \exp(-K_1 t^{n_1})] + w_2 K_2 n_2 \int_0^t [1 - \exp(-K_1\theta^{n_1}) \times](t-\theta)^{n_2-1}\exp[-K_2(t-\theta)^{n_2}]d\theta \tag{4}$$

where $w_1 + w_2 = 1$, indicating that the relative crystallinity at infinite time is unity which corresponds to the Avrami model hypotheses [24]. Values of weight factors provide the relative importance between both crystallizations. It can be noticed that Equation (4) differs from Hsiao et al. [12] model which could be due to a misprint in their article for the derivative of the secondary crystallization in Equation (2).

This paper aimed to investigate the isothermal crystallization kinetics of PEKK 60/40 with a modified Hillier model for crystallization from the melt and cold crystallization to predict precisely the crystallinity evolution according to processing cycles. Basing on experimental data, parameters associated to the modified Hillier model will be assessed carefully and their physical meanings will be discussed. Finally, Time-Temperature-Transformation (TTT) diagrams of the relative volume crystallinity will be built from the overall crystallization modeling.

2. Experimental

2.1. Material and preparation

PEKK used in this study was provided by Arkema referenced as PEKK 6002. It was prepared from diphenyl ether (DPE), terephthalic acid (T) with para phenyl links and isophthalic acid (I) with meta phenyl links with a T/I ratio of 60/40 (Fig. 1). PEKK 60/40 has a weight-average molecular weight (Mw) of about 60000 g mol^{-1}. PEKK samples were supplied amorphous with no crystalline traces measured by DSC and WAXS. The glass transition and melting temperatures were respectively measured about 155 °C and 292 °C by DSC with a heating stage at 10 °C/min.

2.2. Differential scanning calorimetry

Isothermal crystallization analyses were carried out in a TA Instruments Q2000 on granules of about 7–8 mg. For cold and melt crystallization, all specimens were first heated at 10 °C.min^{-1} from room temperature to 360 °C during 5 min. This temperature is above the PEKK 60/40 equilibrium melting temperature (T_{m0} = 340 °C [9]) to erase the thermal history and obtain a fully amorphous polymer. For crystallization from the melt, specimens were then cooled at 40 °C.min^{-1} to annealing temperatures during 120 min and finally cooled to room temperature at 40 °C.min^{-1}. During the cooling steps, the polymer does not have enough time to crystallize and the annealing time is long enough to allow the polymer to fully crystallize. For cold crystallization, the polymer is cooled at 40 °C.min^{-1} to room temperature and then heated at 80 °C.min^{-1} to the isothermal temperature during 120 min and finally cooled at 40 °C.min^{-1} to room temperature. For all specimens after crystallization, a heat scan at 10 °C.min^{-1} to 360 °C was carried out to measure the glass transition, the melting temperature and the melting enthalpy induced by the crystallization cycle.

2.3. Wide-angle X-ray diffraction

The X-ray data were collected by performing wide angle X-ray scattering (WAXS) patterns at room temperature on samples with a thickness of 2 mm thanks to the SAXS/WAXS system from Xenocs. The apparatus consists of an X-ray source using a copper anode K_α radiation with a wavelength of a 1.54 Å delivering a parallel beam. The X-ray patterns were recorded with a MAR300 2D detector

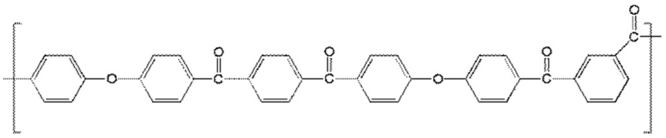

Fig. 1. Chemical structure of PEKK copolymers.