Gibran da Cunha Vasconcelos
Univ. Estadual Paulista
Guaratinguetá – Brazil
mat06070@feg.unesp.br

Rogerio Lago Mazur
Univ. Estadual Paulista
Guaratinguetá – Brazil
rogermaz@uol.com.br

Edson Cocchieri Botelho
Univ. Estadual Paulista
Guaratinguetá – Brazil
ebotelho@feg.unesp.br

Mirabel Cerqueira Rezende
Institute of Aeronautics and Space
São José dos Campos- Brazil
mirabel@iae.cta.br

Michelle Leali Costa*
Univ. Estadual Paulista
Guaratinguetá – Brazil
michelle@feg.unesp.br

* author for correspondence

Evaluation of crystallization kinetics of poly (ether-ketone-ketone) and poly (ether-ether-ketone) by DSC

Abstract: *The poly (aryl ether ketones) are used as matrices in advanced composites with high performance due to its high thermal stability, excellent environmental performance and superior mechanical properties. Most of the physical, mechanical and thermodynamic properties of semi-crystalline polymers depend on the degree of crystallinity and morphology of the crystalline regions. Thus, a study on the crystallization process promotes a good prediction of how the manufacturing parameters affect the developed structure, and the properties of the final product. The objective of this work was to evaluate the thermoplastics polymers PEKK e PEEK by DSC, aiming to obtain the relationship between kinetics, content, nucleation and geometry of the crystalline phases, according to the parameters of the Avrami and Kissinger models. The analysis of the Avrami exponents obtained for the studied polymers indicates that both showed the formation of crystalline phases with heterogeneous nucleation and growth geometry of the type sticks or discs, depending on the cooling conditions. It was also found that the PEEK has a higher crystallinity than PEKK.*
Keywords: *Crystallinity, PEKK, PEEK, DSC.*

LIST OF SYMBOLS

$x(t)$	Volume fraction occupied by the crystallites
k	Constant rate of global crystallization
n	Avrami expoent
E	Activate energy
R	Gas constant
T	Temperature
T_p	Temperature of peak crystallization
ϕ	Ratio of the system colling
ΔH_{fA}	Range of fusion enthalpy of a sample with unknown crystallinity percentage
$\Delta H_{fA\ 100\%\ crystalline}$	Range of fusion enthalpy of a sample with crystallinity of 100%
$(dx/dt)_p$	Variation rate at the peak of crystallization

INTRODUCTION

In recent years, the fast development in science and technology of materials has improved the production of new products in the aerospace industry. Among them the advance in polymeric composites are an example of recognized success. The most commonly used polymer matrices in the processing of structural composites are thermosetting type. However, nowadays new generations of high performance thermoplastic matrix are being developed for use in composites reinforced with carbon fibers.

These matrices have in common high mechanical resistance, thermal and chemical strength (Canevarolo, 2004; Lucas, 2001; Thornburrow, 2000).

The thermoplastic and thermoset polymers differ in many ways. One difference is that it is only possible obtaining some degree of crystallinity in the thermoplastics polymers. The thermosets ones are always amorphous with very low or no crystallinity. The crystallinity consists of regions of aligned polymer chains, usually produced by a single chain bending.

The relationship between crystalline and amorphous region of a polymer sample is expressed in terms of percentage of crystallinity or degree of crystallinity. The percentage of crystallinity of a polymer can be determined by differential scanning calorimetry (DSC), from a peak of exothermic crystallization (Lucas, 2001; Denault, 1996).

DSC is a thermal analysis technique that measures the difference in energy provided to a sample and a reference material in function of a controlled temperature programming. This technique keeps constant the heat supplied to the sample and reference. A control system (servo system) immediately increases the energy supplied to the sample or the reference, depending on if the process involved is endothermic or exothermic. Therefore, the equipment keeps the sample and the

reference at the same temperature. The record of the DSC curve is expressed in terms of heat flow *versus* temperature or time (Lucas, 2001).

During the manufacture of semi-crystalline thermoplastic composites, the polymers are exposed to repeated processes of melting, cooling and crystallization. The knowledge of the crystallization mechanisms of polymers presents a fundamental importance, since the degree of crystallinity influences the mechanical and thermal properties of these materials (Canevarolo, 2004; Lucas, 2001).

The poly (aryl ether ketone) is used as matrices in advanced composites for high performance due to its excellent thermal and mechanical properties. Poly (ether-ether-ketone) (PEEK) and poly (ether-ketone-ketone) (PEKK) offer excellent chemical resistance and good chemical and physical properties at high temperatures. Recently, they have been widely used in commercial applications, where high temperatures and resistance are required (Gardner, 1990; Wang, 1997).

Most physical, mechanical and thermodynamic properties of semi-crystalline polymers depend greatly on the degree of crystallinity and morphology of the crystalline regions. The higher the crystallinity, the higher are the properties of density, stiffness, dimensional stability, chemical resistance, abrasion resistance, melting temperature and glass transition temperature. Therefore, detailed knowledge of crystallization kinetics in a transformation processes is fundamental to control the final properties of the composites (Canevarolo, 2004; Lucas, 2001).

Traditionally, the more widely used technique in crystallization kinetics is DSC. With different analysis parameters, DSC can provide important characteristics for the studied polymer, and it is possible to achieve different mechanical characteristics at the same polymer to different applications (Lamberti, 2006).

Several researchers have been studying the crystallization kinetics of thermoplastic polymers with high structural performance. The Avrami kinetic model, developed at first from the probability theory, is simple and yet enough complete to describe the nucleation and growth until the crystals collision. The Avrami model describes the macroscopic nucleation and growth of any crystal structure as a function of time. In general development, it is assumed that the time of nucleation and crystal growth are interdependent and depend on distribution of material to areas of growth of crystallites. The final expression for isothermal crystallization is given by Eq. 1 (Lucas, 2001; Hsiao, 1991; Ferrara, 2004):

$$X(t)=1-\exp(-kt^n) \qquad (1)$$

If we multiply both sides of the Eq. 1 by (ln), we get (Eq. 2):

$$\ln(\exp(-kt^n))=\ln(1-x(t)) \qquad (2)$$

Regrouping the Eq. 2 and multiplying again by (ln), we have (Eq. 3):

$$\ln(-\ln(1-x(t))=\ln(k)-n\ln(t) \qquad (3)$$

Therefore, if we plot the axis $\ln(-\ln(1-x(t)))$ *versus* $\ln(t)$, the angular coefficient of the formed straight line gives us directly the value of the Avrami exponent.

The Avrami exponent describes the crystallization and provides qualitative information about the nature of the process of nucleation and crystal growth. The relationship between the constant of crystallization kinetic and the activation energy is given by Eq. 4 (Lucas, 2001; Canevarolo, 2004):

$$k=k_0.\exp\left(\frac{-E}{R.T}\right) \qquad (4)$$

Therefore, the Avrami exponent may be calculated by (Eq. 5):

$$n=\left(\frac{dx}{dt}\right)_p R.Tp^2.(0{,}37.\varnothing.E)^{-1} \qquad (5)$$

The activate energy might be calculated (Eq. 6) by knowing the temperature of crystallization peak, from Eq. 5:

$$\ln\left(\frac{Tp^2}{\varnothing}\right)=\frac{E.Tp}{R}+cte \qquad (6)$$

So, the crystallization percentage is calculated directly by (Eq. 7) (Lucas, 2001; Sidel, 2008):

$$\% \text{ of crystallization} = \frac{\Delta H_{fA}}{\Delta H_{fA\ 100\%\ cystalline}} \times 100 \qquad (7)$$

The objective of this paper was to initiate a study of the crystallization kinetics of PEEK and PEKK polymers by DSC, in order to get the relationship between the kinetics, the percentage, the nucleation and the geometry

of crystalline phases formed, according to the parameters of Avrami and Kissinger models.

METHODOLOGY

Materials

In this study, the semi-crystalline thermoplastic polymers PEKK and PEEK were analyzed. The used PEKK was supplied by Du Pont company in the form of granules, and PEEK was manufactured by the company ICI and negotiated by LATI® thermoplastics in powder form.

Study of crystallization kinetics

PEKK

The analysis by DSC was performed in a Perkin-Elmer Pyris 1 Model – DSC, calibrated with indium and zinc, under constant flow of nitrogen (20 mL/min) and a heating rate of 20°C/min. Samples of PEKK (~ 15 mg) were encapsulated in a standard sample pan of aluminum. Firstly, a dynamic analysis (30 to 380°C at 20°C/min, followed by cooling at the same rate) was performed in order to know the melting and crystallization temperatures of PEKK. Then, new samples were prepared and heated at a heating rate of 20°C/min from ambient temperature to the thermodynamic melting temperature of PEKK (~ 340ºC), remaining 2 minutes at this temperature to allow complete melting of all crystals (thus eliminating that remaining crystals which act as seeds for crystallization). Subsequently, the samples were cooled under the rate of 100°C/min until the desired isothermal temperatures of crystallization (305°C, 307°C, 310°C and 311°C) and were maintained in these isothermals until the formation of the exothermic peaks of crystallization.

PEEK

The DSC analysis was performed in an equipment SII NanoTechnology Inc. – Seiko Model EXSTAR6000, previously calibrated with indium and zinc, at a heating rate of 10ºC/min. Samples of PEEK (~ 10 mg) were encapsulated in a standard pan sample of aluminum, and dynamic analyses were carried out at temperatures of 50°C to 380°C. The samples were heated in the heating rates of 5, 10, 15 and 20°C/min. Subsequently, these samples were cooled at the same rates used for heating until the temperature of 50°C, in order to forming exothermic

peaks which determine the existence of crystalline phases in the polymer.

From these curves, it was possible to establish the kinetic parameters of crystallization, with consequent study on the type of nucleation involved in the formation of crystalline phases and the geometry of their growth. This study was based on the kinetic modeling of Avrami and Kissinger.

RESULTS AND DISCUSSION

PEKK

In this study, the sample was heated twice in the DSC, according to the norm ASTM D3418, in order to destroy the thermal history of the polymer; only the second heating was considered for data analysis. Figure 1 shows the second dynamic heating of PEKK, where an endothermic peak can be observed in the curve at the temperature of 314°C, indicating the melting of the material. The endothermic peak generated a fusion enthalpy of 6.9 J/g.
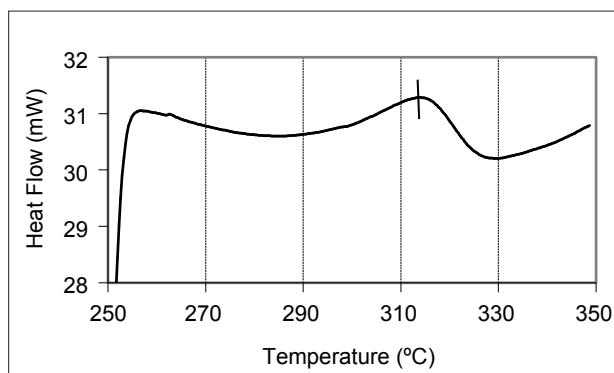

Figure 1:   DSC of the second heating cycling of PEKK on a rate of 20°C/min.

According to the literature, the melting temperature of PEKK is around 305-340°C; however, these values are directly related to the rate which the polymer is cooled or heated (ratio of heating, cooling, isotherms) and factors such as the processes involved in the synthesis of the polymer. This makes harder a direct comparison between the data. Even though, the melting temperature found in this study is within the range described in the literature (Hsiao, 1991; Pratte, 2002; Vries, 2006; Salek, 2005).

Then, the PEKK was cooled in a rate of 100ºC/min, until four different temperatures, all in the melting region of PEKK. Samples were kept in the isotherms for 60

minutes, in order to obtain the organization of polymeric macromolecules for the formation of crystalline phases. Thus, an exothermic peak on the crystallization (Tc) should be clearly observed.

The crystallinity (about 5.4%) was obtained from the ratio between the fusion enthalpy of the sample (ΔH_{fA}) and the fusion enthalpy of 100% crystalline sample (ΔH_{fA} 100% crystalline) according with Eq. 7. Table 1 shows that the exothermic peaks obtained at the chosen isothermal crystallization of 305°C, 307°C, 310°C and 311°C showed low enthalpy.

Table 1: Crystallization enthalpy values of PEKK for the 305, 307, 310 and 311°C isotherms

Isotherms (°C)	$-\Delta H$ (J/g)	$t_{1/2}$* (min)	Crystallization rate (%)**(min⁻¹)
305	0.915	0.2	5
307	1.647	0.21	4.76
310	0.794	0.24	4.16
311	0.317	0.22	4.54

* $t_{1/2}$ is the necessary time to achieve half of crystallization, or the necessary time to achieve the peak at the crystallization curve on DSC.
** Crystallization rate (%) is defined as 1/ $t_{1/2}$.

It appears that in none of the studied isothermals the crystallization was complete, since the values of enthalpy are smaller from that obtained for the dynamic fusion of PEKK. This can also be explained based on the low crystallinity of PEKK, which makes difficult the crystallization process in the crystalline melt region. The enthalpy values are very close, with the exception of the isotherm at 311°C, which is the isotherm of the highest temperature and probably makes difficult the formation of crystals. The half life times obtained for each isotherm (Table 1) are also similar and show a very fast rate of crystallization: less than 0.2 minute. It must be remembered that high crystallization rate is not directly related to high degree of crystallinity (Hsiao, 1991). The highest rate was achieved in crystallization isothermal of 305°C.

Figure 2 shows the experimental points obtained from the isotherms (symbols) and the mathematical fit used by the regroup of Avrami equation (Eq. 3). The good correlation between the experimental points and the lines shows that the Avrami equation model fits the crystallization kinetics of PEKK. The values of Avrami exponent (n) were about 2.7 and 2.0 for the isotherms of 310 and 307°C, respectively. This indicates that the PEKK at

these temperatures has crystal growth geometry of disk type with heterogeneous nucleation, as suggested in the literature (Lucas, 2001).
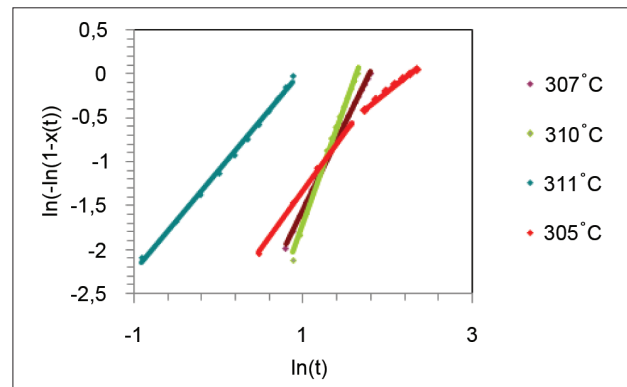

Figure 2: Relation between the experimental peaks and the math model (straight lines) of Avrami used.

In the 305°C isotherm, we observed that the kinetic behavior of PEKK shows a double kinetic feature, where there is a primary and a secondary stage, as observed by Velisaris and Seferis (1986), among others, suggesting the existence of two active mechanisms in crystallization process. At this temperature, the first stage of crystallization has a value of n of about 1.4 and the second one has a value of 0.66 (Hsiao, 1991, Ferrara, 2004, Velisaris; Seferis, 1986).

Figure 3 shows the development of relative crystallization (α in %) with the isothermal crystallization time for the temperatures of the rigid crystalline phase and variable amorphous phase between 305 and 311°C. It can be observed in the deform S format of graphs that the crystallinity (%), initially zero, begins to grow rapidly
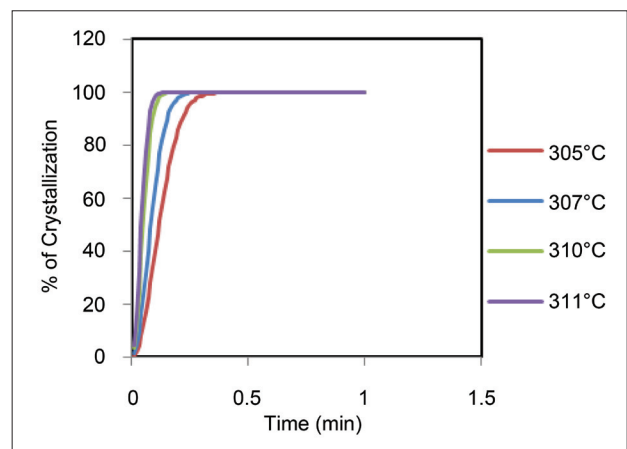

Figure 3: Development of crystallization relative to isothermal crystallization time for temperatures from 305 to 311°C.

in the first few moments of crystallization, achieving quickly 100% of crystallization for this material – remembering that PEKK has low crystallinity (< 6%) (Wang, 1997). It appears that, with the increasing of temperature, the isothermal crystallization process becomes greatly accelerated in reaching complete crystallization in less than 30 seconds. This fact makes difficult the study of isothermal crystallization kinetics for PEKK, since the control of crystallinity of the material is complex due to the high spontaneous crystallization process.

PEEK

The PEEK was first heated until its melting and then cooled at the rates of 5, 10, 15 and 20°C/min. Figure 4 shows the exothermic peaks formed during the cooling of PEEK, and the values of enthalpy of crystallization for these peaks are shown in Table 2. It can be observed that the greatest crystallization enthalpy for this polymer was found for the cooling rate of 20°C/min. This shows that the crystallinity of this polymer is promoted by higher cooling rates.
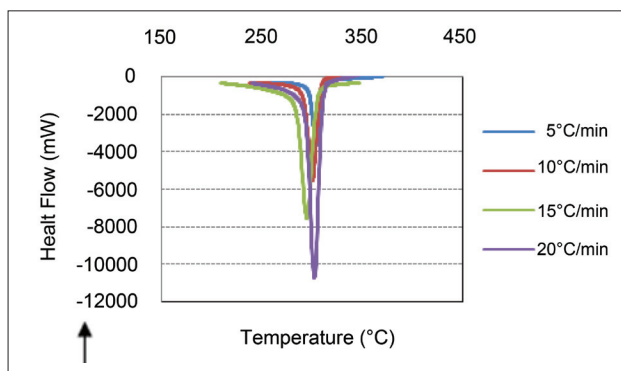
Using the values of the crystallization temperature peak of Fig. 4, the DSC curves for various cooling rates were linearized using the method of least squares applied for Gaussian functions. The values of crystallization peak temperature for the studied cooling rates are shown in Table 3.

Table 3:   Temperatures of crystallization peak found to the different cooling rates of PEEK

Cooling rate (ºC/min)	Crystallization peak temperature (ºC)
5	303.5
10	299.4
15	293.4
20	291.2

From Table 3, it was possible to obtain the curve of $\ln(T_p^2/\phi)$ *versus* $1000/T_p$, which gives the curve fit by the least squares method, shown in Figure 5.
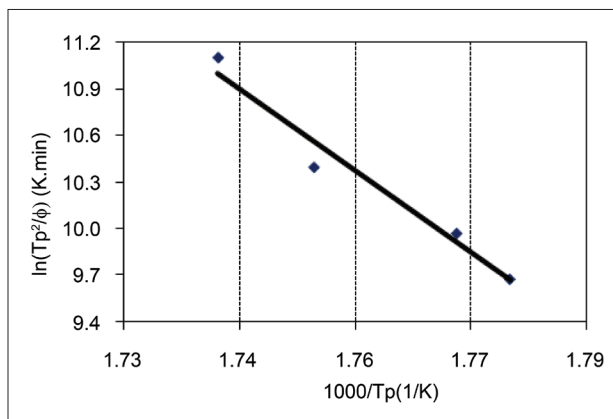

Figure 4:   DSC curves of PEEK for the following heating rates: 5, 10, 15 and 20°C/min.

Figure 5:   Graph of $\ln(T_p^2/\phi)$ *versus* $1000/T_p$ to the heating rates of 5, 10, 15 and 20 °C/min to the PEEK.

Table 2:   Enthalpy values found to the different cooling rates of PEEK

Cooling rates (°C/min)	ΔH (J/g)
5	-45.8
10	-37.7
15	-45.5
20	-53.8

From Fig. 5 and Eq. 6, it was possible to calculate the activation energy (E) for crystallization of PEEK. The value of E, calculated following the Kissinger modeling, was 292.5 kJ/mol.

Knowing the crystallization enthalpy, obtained from Fig. 4, the curve of the fraction of crystallized material as a function of reaction time, using Eq. 6, was possible to obtain. Figure 6 shows the required time to complete the crystallization reaction of PEEK in different ratios of cooling in which it was submitted.
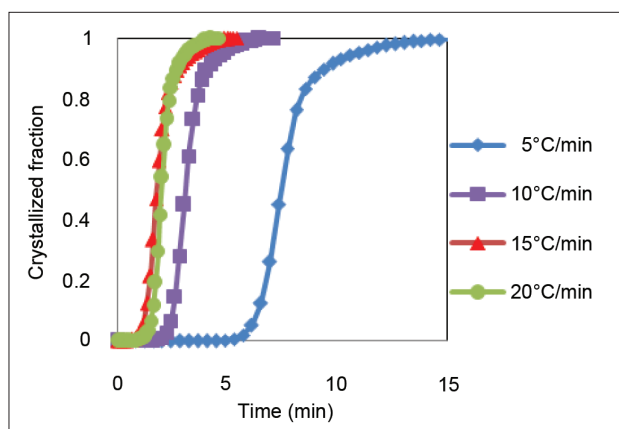
Figure 6: Crystallizated material fraction *versus* time to the heating rates of 5, 10, 15 and 20°C/min.

The crystallization rate (dx/dt) of PEEK was obtained from the fraction of crystallized material at the various cooling rates involved (Fig. 7). The growth rate shows the points where the crystallization occurred in a higher rate. The largest variation obtained for each curve is used to determine the value of n for different cooling rates in which the material was submitted.
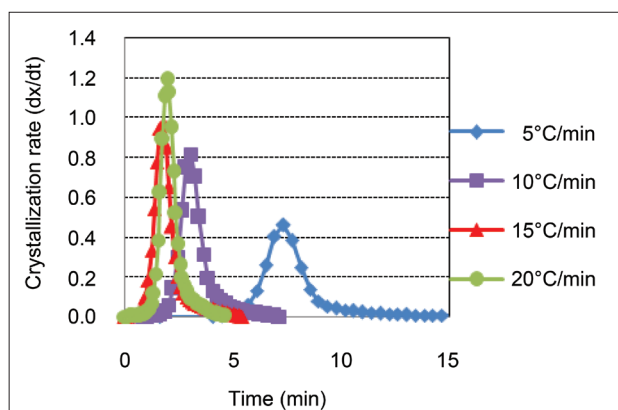

Figure 7: Curves of crystallization rate *versus* temperature to PEEK for the heating rates: (a) 5°C/min; (b) 10°C/min; (c) 15°C/min; (d) 20°C/min.

Knowing the value of E involved in the crystallization process, the value of n for the PEEK was calculated from Eq. 5.

The value of n is related to the growth geometry of crystalline phases and also with this type of nucleation. Thus, at the cooling rates of 5 and 10°C/min, the crystalline phases were formed with heterogeneous nucleation and growth geometry of disk type. For the cooling rates of 15 and 20°C/min, the crystalline phases were also formed with heterogeneous nucleation;

however, the growth geometry formed was the bat type (Lucas, 2001).

Table 4 summarizes data from the value of n found for cooling rates studied for PEEK.

Table 4: Avrami exponent values found for the different cooling rates to PEEK

Cooling rate (°C/min)	Avrami exponent (n)
5	2.35
10	2.06
15	1.59
20	1.46

CONCLUSIONS

For the isothermal temperatures of 307 and 310°C, the Avrami model fits the crystallization kinetics of PEKK, which allows the study of the crystal growth geometry in this region. The value of n is obtained in the range from 2.0 to 2.7, with heterogeneous nucleation, which indicates a growth type of disc geometry.

For the isotherm of 305°C, the PEKK exhibited a double kinetic behavior, with probably two active mechanisms in the process of crystallization. At this temperature, the first stage of crystallization showed a value of n of about 1.4, indicating a stick growth-type geometry with heterogeneous nucleation, but in the second stage the model does not fit the kinetics of crystallization.

The deformed S shape, observed in the relation of crystallization relative to time of isothermal crystallization, shows that the accelerated crystallization process makes difficult the study of PEKK crystallization at the isothermals chosen.

The PEEK showed significant crystallinity in all the studied cooling rates. Moreover, it was observed that the crystallization time for this polymer is between about 5-15 minutes. That means that, in order to promote the crystallization of this polymer, is not necessary to maintain it at high temperatures for too long.

Thus, the crystallization process is not too fast, which may cause a difficulty in controlling the process and makes not possible to obtain parts with a high degree of crystallization in very short periods of time. It can be also observed that the growth geometry of disc type in PEEK is promoted by lower cooling rates. Major cooling rates promotes the growth geometry of the bat type.

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It was possible to obtain the correlation between the crystallization kinetics of both studied polymers. Thus, a much higher crystallinity in the case of PEEK was primarily noted.

Furthermore, the formation of crystalline phases for PEKK occurred in a more spontaneous way when compared with PEEK.

This suggests that there is a difficulty in controlling the crystalline fraction of PEKK, comparing to PEEK.

The analysis of the obtained n values indicates that both polymers showed the formation of crystalline phases with growth geometries of bat or discs types, depending on the cooling conditions applied. The study of crystallization kinetics of PEKK was held in a restricted manner, due to the difficulty of crystallization of this polymer and its low crystallinity. Thus, it was possible to study the crystallization kinetics for this polymer only under isothermal conditions.

As it was possible to obtain significant crystallinity for PEEK with relative easiness, the study of this polymer occurred in the form of dynamic tests. However, an analysis under isothermal conditions as a complement to the previous study should be also performed. Moreover, for a possible application of this polymer, its degradation kinetic should also be studied, as it would promote parameters for "lifetime" of the material at temperatures in which it is applied.

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