Influence of the melt temperature
on the thermoplastics crystallization process

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SUMMARY

The influence of the melt temperature (T_1) on the crystallization kinetics and the morphology of two semicrystalline polymers : poly(oxymethylene) : $T_m^o = 198°C$ and poly(ether-ether-ketone) $T_m^o = 380°C$) was investigated using thermal analysis and optical microscopy. For different melt temperatures (T_1), isothermal and nonisothermal crystallizations were analysed using the AVRAMI and OZAWA models.

Using different analyses, for both polymers we observed a spherulitic growth with the following influence of the melt temperature on the number of spherulites :

- $T_1 < T_m^o$ produces many small spherulites
- $T_1 > T_m^o$ gives rise to few large spherulites

KEYWORDS : Poly(oxymethylene), Poly(ether-ether-ketone), DSC, Kinetics, Melt temperature, Crystallization.

INTRODUCTION

Semi-crystalline polymer is made by two different phases (amorphous and crystalline). The induced properties are function of the crystallinity rate, the lamellar thickness and the spherulitic size. But all these structural parameters depend on the processing conditions :

- thermodynamics parameters : temperatures, cooling rates...
- mechanical parameters : shearing rates, drawing rates...

The purpose of this paper is the understanding of the influence of the thermodynamic parameters on the crystallization mechanism. Two semi-crystalline polymers were studied : the poly(oxymethylene) (POM) from Du Pont de Nemours and the poly(ether-ether-ketone) (PEEK) from ICI. POM is a homopolymer with a high crystallinity ratio (60 to 80 %) and a melting temperature of $T_m \sim 175°C$. PEEK is a semi-crystalline polymer

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(few pourcent to 48 % of crystallinity) with a glass transition $T_g \sim 145°C$ and a melting temperature $T_m \sim 335°C$. PEEK can be also found amorphous but only under film shape. The crystallization kinetics (isothermal and nonisothermal) were analysed by AVRAMI and OZAWA equations, as a function of the melt temperature (T_1). It will be shown that T_m^o (equilibrum melting temperature) could be an important parameter. DSC and optical microscopy were used for this study.

RESULTS AND DISCUSSION

Isothermal crystallization

The AVRAMI equation (1-4) is used for analysing the isothermal crystallization :

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

where : $\alpha_v(t)$ is the relative crystallinity in volume at the time t, n and k are the AVRAMI exponents and t the time in second. The exponent n depends on the mechanism of nucleation and the crystal growth geometry (5) and k is a constant including the nucleation density and growth rate. The equation (2) is used for determining the parameters n and k :

$$\ln(-\ln[1-\alpha_v (t)]) = n \ln t + \ln k \qquad (2)$$

Then, n and k are respectively estimated from the slope and the intersection of the plot of $\ln(-\ln[1-\alpha_v(t)]$ versus ln t. This evaluation is realized for the two polymers (POM and PEEK) as a function of the melt and crystallization temperature. The results are reported in table 1.

POM			PEEK			
$T_1(°C)$	$T_c=152°C$	$T_c=156°C$	$T_1(°C)$	$T_c=305°C$	$T_c=315°C$	
185°C	2.3	2.5	365°C	3.0	3.0	n
	$1.36 \ 10^{-5}$	$1.4 \ 10^{-8}$		$2.3 \ 10^{-6}$	$3.0 \ 10^{-8}$	k
205°C	2.4	2.7	410°C	3.5	3.3	n
	$6.1 \ 10^{-6}$	$3.4 \ 10^{-9}$		$8.3 \ 10^{-8}$	$3.3 \ 10^{-9}$	k

These results showed that n seems to be independent of the crystallization temperature T_c for the two polymers and a little bit dependent on the melt temperature (T_1) only for the PEEK. For the two polymers these values are interpreted by a athermal nucleation followed by a spherulitic growth (observed by optical microscopy). But we observe : n(POM)<n(PEEK). The

spherulitic size of POM is very large (diameter > 100 μm), so that a lot of spherulites are truncated and induced a depress value of n (6). Table 1 shows that k decreases as T_1 increases. This point could be explained by the evolution of the persistance of small crystalline impurities which are stable above the nominal melting temperature (7). Moreover the difference $k_{Tc}(T_1 < T_m^{\circ}) - k_{Tc}(T_1 > T_m^{\circ})$ for the POM is lower than the PEEK.

Anisothermal crystallization

Differential Scanning Calorimeter study

The polymers were cooled from the melt temperature (T_1) at a constant cooling rate (T = $-20°$C/min for the POM and T = $-40°$C/min for the PEEK) under nitrogen atmosphere.

In figure 1, we can observe that as the melt temperature (T_1) increases, the crystallization temperature is shifted to lower temperatures.
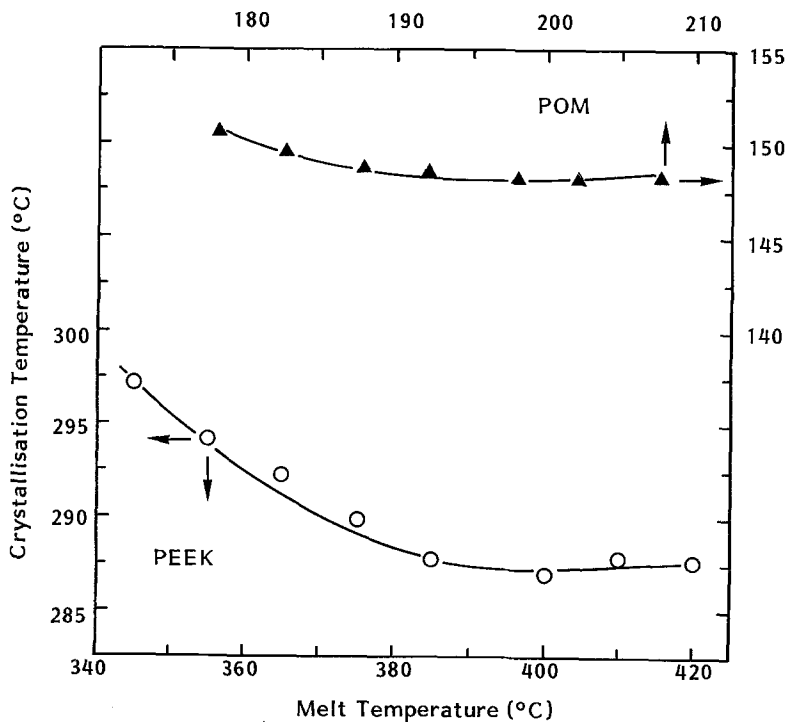

Figure 1 : Evolution of the crystallization temperature, T_c, versus melting temperature T_1, for the PEEK (o) and for the POM ( ).

Moreover the shape of the both curves is very similar and could be separated as two portions : for $T_1 < T_p$, T_c decreases

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as T_1 increases, and for $T_1 > T_p$, T_1 is nearly constant as T_1 increases. For the two polymers the value of T_p is very close to the equilibrum melting temperature :

- for the POM : T_p = 192°C and T_m^o = 198°C   (8)
- for the PEEK : T_p = 385°C and T_m^o = 380°C   (8)

This phenomenon could be attributed to the number of nuclei which decreases for $T_1 < T_p$ and is constant for $T_1 > T_p$.

Microscopic observations and nonisothermal crystallization kinetic (OZAWA theory's) - Comparative study.

The number of spherulites as a function of the melt temperature is observed with a polarizing microscope under a hot stage. Figure 2 represents this evolution for the POM.

From this figure we can define a ratio R as follows :

$$R = \frac{\text{number of spherulites at } T_1 = 185°C}{\text{number of spherulites at } T_1 = 205°C} = 5.3$$
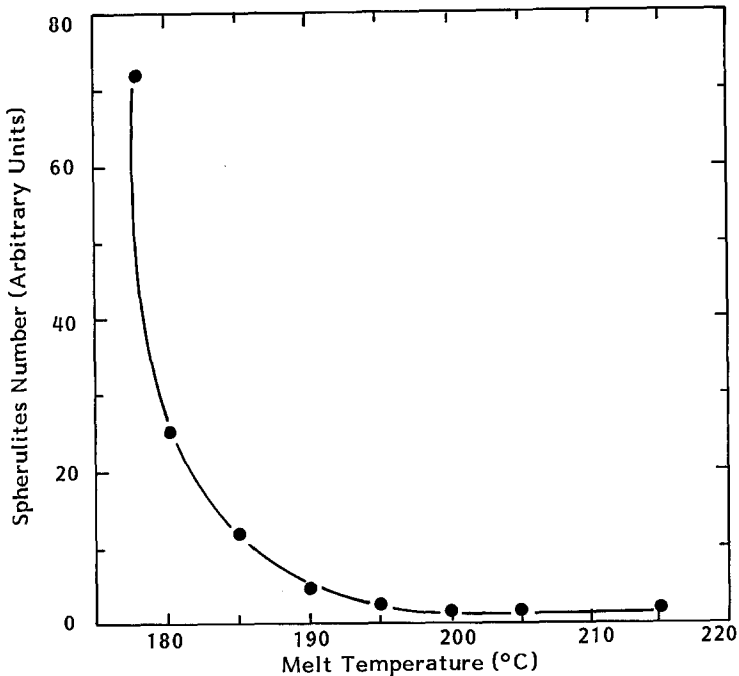

Figure 2 : Variation of the number of spherulites (in arbitrary cross-section unit) versus the melting temperature T_1, for the POM.

The nonisothermal crystallization kinetic developped by OZAWA (9) is a mathematical derivation of the EVANS equation :

$$\ln((1-\alpha_v) = -K(T)/T^n \qquad\qquad (3)$$

where α_v is the relative crystallinity in volume, $K(T)$ is a cooling or heating function ($°C/min$)^n and T the heating or cooling rate ($°C/min$). The nonisothermal crystallization is performed at different cooling rates :

- 1°C/min to 20°C/min for the POM
- 7°C/min to 40°C/min for the PEEK.

The plot of $\ln(-\ln[1-\alpha_v])$ versus $\ln(T)$ would result in a series of parallel lines of slope, n, and intercept $\ln K(T)$. An extension of the OZAWA theory (10) permits to evaluate the ratio of the activated nuclei number during the crystallization for two melt temperatures (T_1), at a given T_c. For the POM, this ratio : $K(T)185°C/K(T)205°C = 6$ is very close to the ratio, R, defined by optical microscopy observation ($R = 5.3$).

Any value could be find for the PEEK, because spherulites are too small (diameter <1μm) to be observed by optical transmission microscopy. But a qualitative analysis shows that the melt temperature influence is greater for the PEEK than for the POM. However, the ratio $R = K(T)365°C/K(T)410°C = 35$ calculated for the PEEK with OZAWA theory's seems to be in good agreement with optical observations.

CONCLUSION

With three different analysis, it is possible to describe the melt temperature (T_1) influence on the spherulite number and their sizes. This study points out the size increasing of spherulites as well as the melt temperature increasing for $T_1 < T_p$. This phenomenon is more marked for the PEEK than for the POM.

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