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NON-ISOTHERMAL CRYSTALLIZATION KINETICS OF HOT DRAWN POLYESTER FILMS

Kissinger and Ozawa analysis

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Abstract

The non-isothermal crystallization kinetics of hot drawn poly(ethylene terephthalate) films were studied using the Kissinger and Ozawa equations. The influence of the initial drawing on the crystallization kinetics was investigated. The values of the apparent activation energy and of the Avrami exponent indicates that the nucleation and growth of crystallites depend greatly on the stress submitted to the samples.

Keywords: crystallization, drawing, kinetics, Kissinger, Ozawa, poly(ethylene terephthalate)

Introduction

Among the plastic materials, the poly(ethylene terephthalate) (PET) is a very useful thermoplastic. Indeed this polymer is easy to obtain in different semi-crystalline states or in a wholly amorphous state and therefore it is particularly well suitable for forming processes. Then it is widely used in fiber, in film as well as in container technologies. Although extensive studies have been performed on the morphology and on crystallization kinetics of unoriented [1, 2] and oriented [3–5] materials, very few results concern thermal crystallizations carried out after a hot stretching involving strain induced crystallization. However, for industrial uses it is very important to known if this primary induced crystallization acts on the thermal one, and how the drawing could modified the kinetics of thermal crystallization. This paper deals with calorimetric investigations carried out by non-isothermal crystallization of homogeneous hot drawn samples and gives new results on the variations of crystallization kinetics with the drawing ratio.

Experimental

After an isothermal annealing (15 min) at 100°C, isotropic (the birefringence is less than 10^{-3}) and amorphous (the absence of an initial crystallinity is

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checked by DSC and wide angle X-ray scattering measurements) PET films (Mn ≅ 31100, Ip ≅ 2) of 500 μm thickness are drawn at a strain rate of 0.14 s^{-1} in a tensile machine equipped with a heating chamber. The draw ratio λ, equal to the ratio of the extensed length on the original length, varies from 1 to 7. The drawing temperature, included between the glass transition temperature and the cold crystallization temperature allows homogeneous drawn and no thermally crystallized samples to be obtained. Then, the material is cold air quenched down to room temperature in order to freeze in its structural state. Finally the different samples for the DSC measurements are punched into the stretched material. The enthalpic analysis are performed on a Perkin Elmer DSC7 at various heating rates (5 to 50 K min^{-1}) between room temperature and melt temperature. Indeed, we have to point out here two factors which limit the experimental domain.

a) already observed, the effect of the hot drawing on the thermal behaviour (Fig. 1) is mainly characterized by: i) the shift of the thermal crystallization temperature range towards the glass transition region; ii) for λ>4 the disappearance of the non-isothermal crystallization (Fig. 4 in Ref. [6] and Fig. 1); iii) the shift of the glass transition temperature to higher temperatures (Fig. 5 in Ref. [6] and Fig. 1).

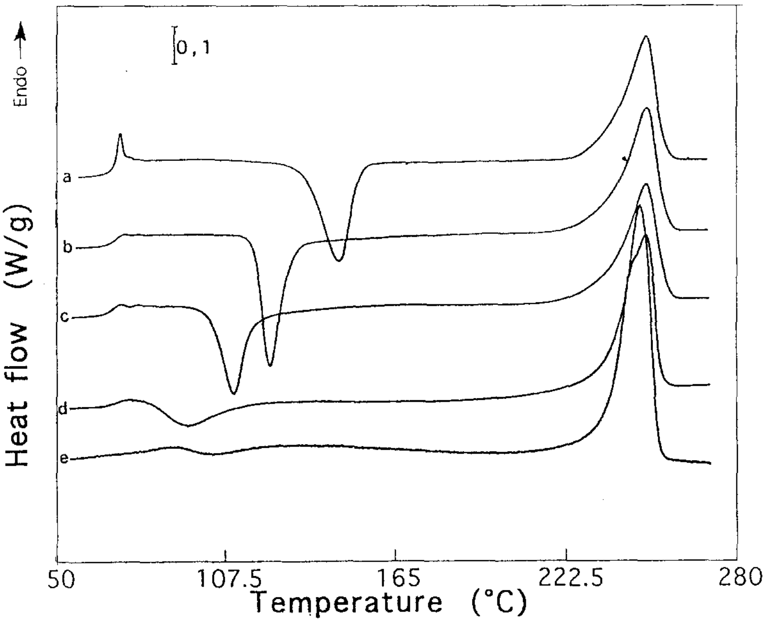

Fig. 1 DSC curves of various PET samples. The diagrams are normalized to 1 g of matter and the heating rate is equal to 7 K min^{-1}. The draw ratios are: a) λ = 1 (undrawn sample); b) λ = 1.4; c) λ = 2; d) λ = 2.8; e) λ = 3.4

Thus, as the position of the crystallization peak depends on the heating rate, the possible range of heating rate will be limited by overlapping of the crystallization peak with the glass transition region (lower rates) as well as with the melting peak (higher rates).

b) The disappearance of the thermal crystallization fixes the upper limit of the studied draw ratio to 4.

Results and discussion

In a previous work [6] we have confirmed by WAXS measurements the appearance of a strain induced crystallized phase for $\lambda \geq \lambda_c = 2.8$. In the present work, we have studied by DSC the non-isothermal crystallization of five different drawn samples, i.e.: $\lambda = 1$ (or non-stretched reference film); $\lambda = 1.4$, $\lambda = 2$ (oriented amorphous samples); $\lambda = 2.8$ and $\lambda = 3.4$ (partially strain induced crystallized samples). Figures 2 and 3 give examples of the experimental scans for $\lambda = 1$ and $\lambda = 3.4$ respectively. Figure 2 shows clearly that the crystallization peak shifts towards the higher temperatures with the increase of the heating rate and that the crystallization and the melting peaks overlap for the greatest heating rate used. The glass transition (around 75°C) does not interfer with the crystallization region for the lowest used heating rates. Figure 3 displays the opposite behaviour. Indeed, the crystallization zone and the glass transition region which have shifted to the lower and the higher temperatures respectively, now interfer for the lowest heating rates whereas there are no constraint for the highest heating rates. Moreover the crystallization region narrows and the crystallization seems to become temperature independent.

As a first approach of the influence of the drawing on the kinetics, we examine the variations of the temperature of the crystallization peak with the heating rate. Open to criticism, the Kissinger representation [7] gives yet a rough idea of this influence. This representation could be described by the following equation:

$$\ln\left[\frac{q}{T_p^2}\right] = \frac{\Delta E_c}{RT_p} + Cst$$

where q is the heating rate and T_p the temperature at the maximum of the crystallization peak.

Thus the plot of $\ln(q/T_p^2)$ *vs.* $1/T_p$ yields a straight line and its slope gives the apparent activation energy ΔE_c of the phenomenom. Figure 4a reports the results obtained for the five studied draw ratios and shows that the crystallization becomes temperature independent for λ greater than 3 (values comparable to the critical drawing ratio $\lambda_c = 2.8$).

On the Fig. 4b which shows the variation of the apparent activation energy with λ, we have also reported the activation energies (■, Δ) measured in the

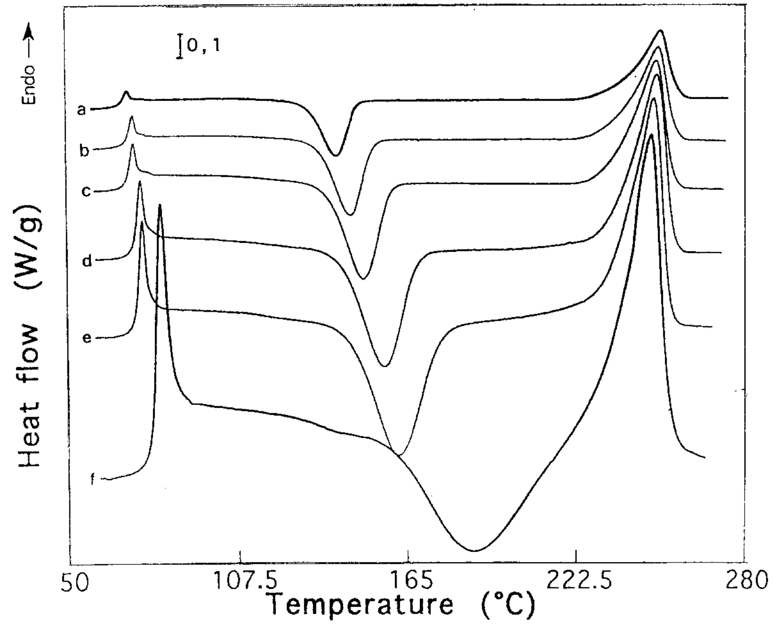

Fig. 2 DSC curves of undrawn samples (λ = 1) at various heating rate: a) 5 K min^{-1}; b) 7 K min^{-1}; c) 10 K min^{-1}; d) 15 K min^{-1}; e) 20 K min^{-1}; f) 50 K min^{-1}

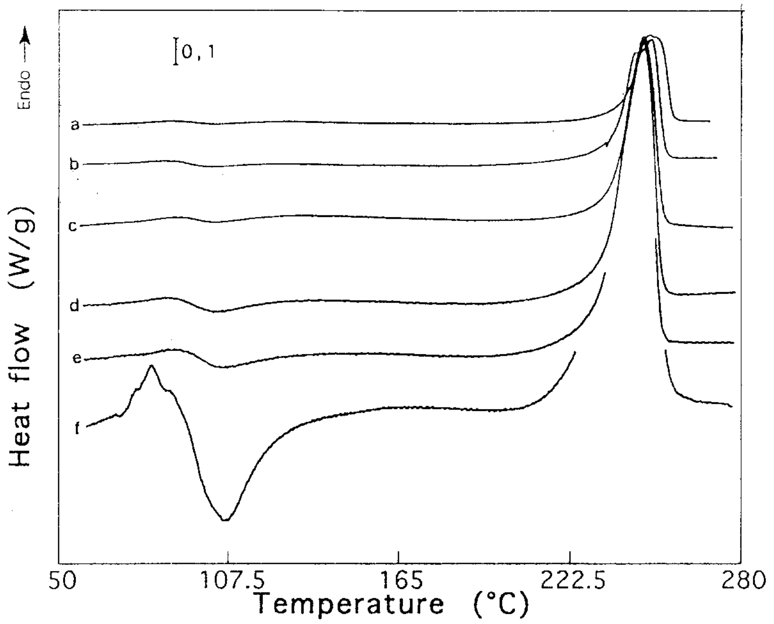

Fig. 3 DSC curves of λ = 3.4 drawn samples at various heating rate: a) 5 K min^{-1}; b) 7 K min^{-1}; c) 10 K min^{-1}; d) 15 K min^{-1}; e) 20 K min^{-1}; f) 50 K min^{-1}

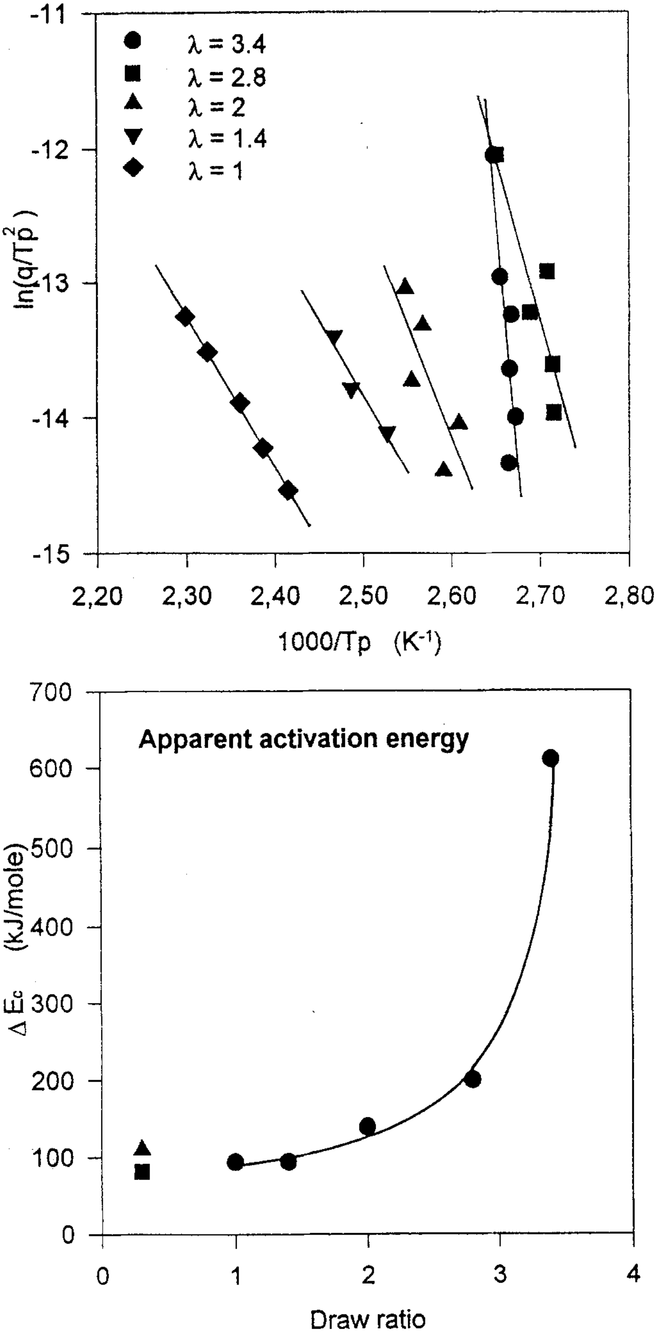

Fig. 4 (a) Kissinger representation: $\ln(q/T_p^2)$ *vs.* $1/T_p$ for the five draw ratios, and (b) variation of the apparent activation energy of crystallization with λ. Extra dots are: ■ bulky amorphous injected PET samples, ▲ commercial PET granules after quenching from the melt

case of the thermal recrystallization of bulky injected PET samples ($Mn \approx 25000$) and of recrystallization after quenching from the melt of commercial PET granules ($Mn \cong 26000$) respectively. For the law draw ratio ($\lambda < \lambda_c$) the activation energy remains constant and equal to its initial value; it lies around 100 kJ mol^{-1}. Moreover for undrawn PET, ΔE_c does not depend on the nature of the sample (average molecular weight, forming process,...). Then the apparent activation energy increases considerably with λ and goes infinite. In terms of activated processus theory, the barrier to cross to reach the crystalline state becomes so high that the crystallization can not be thermally stimulated. In a first time, it becomes heating rate independent ($2.8 < \lambda < 5$) and after it vanishes ($\lambda > 5$).

Secondly, in order to obtain pertinent kinetic parameters, we applied the non-isothermal Ozawa's theory whose has been tested to the crystallization of different PET samples [8, 9]. This theory could be described by the following equation:

$$X = 1 - \exp(-\chi(T)\, q^{-n})$$

this equation can be written as:

$$\ln(-\ln(1 - X)) = \ln(\chi(T)) - n\ln(q)$$

where X is the rate of transformation, $\chi(T)$ is a function of the heating process, n is the Avrami exponent depending upon the geometry of nucleation and growth. The $(1-X)$ values can be obtained directly from DSC measurements at heating rate q.

The plot of $\ln(-\ln(1 - X))$ *vs.* $\ln(q)$ yields straight lines for different temperatures thus values of n (slope) and $\ln(\chi)$ (intercept) for these temperatures can be obtained. For example, Figs 5a and 5b shows this representation for $\lambda = 1$ and $\lambda = 3.4$ respectively. Variations of n and $\ln(\chi)$ with the temperature are presented for the five draw ratios in Figs 6a and 6b respectively.

Its appears that the values of the Avrami exponent decrease with the temperature for the wholly amorphous samples (oriented or not) while for the partially strain induced crystallized samples, n is practically independent of the temperature. The variation of n was attributed to a change in the nucleation behaviour [10]: at low temperatures, nucleation was sporadic in time, while at high temperatures it was instantaneous. At a given temperature, drawing leads to a general decrease of n. Moreover for the strain induced crystallized samples, the values of n become very small (between 0 and 0.5) showing that the spherulitic crystallization has disappeared. It is confirmed by the variation of $\chi(T)$ with the temperature and with the draw ratio. The mechanism of crystallization changes with the initial drawing: from a three dimensional growth for

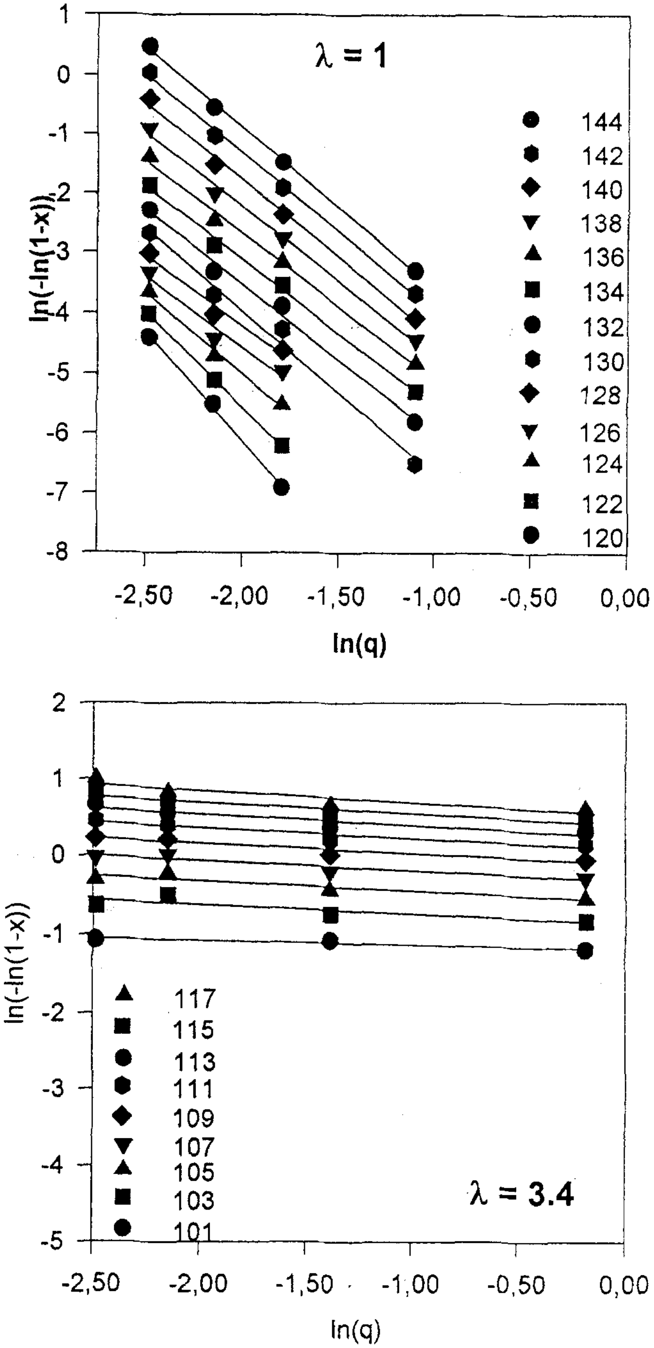

Fig. 5 Plot of ln(−ln(1 − X)) *vs*. ln(q) for different temperatures (in °C) corresponding to (a) $\lambda = 1$; (b) $\lambda = 3.4$

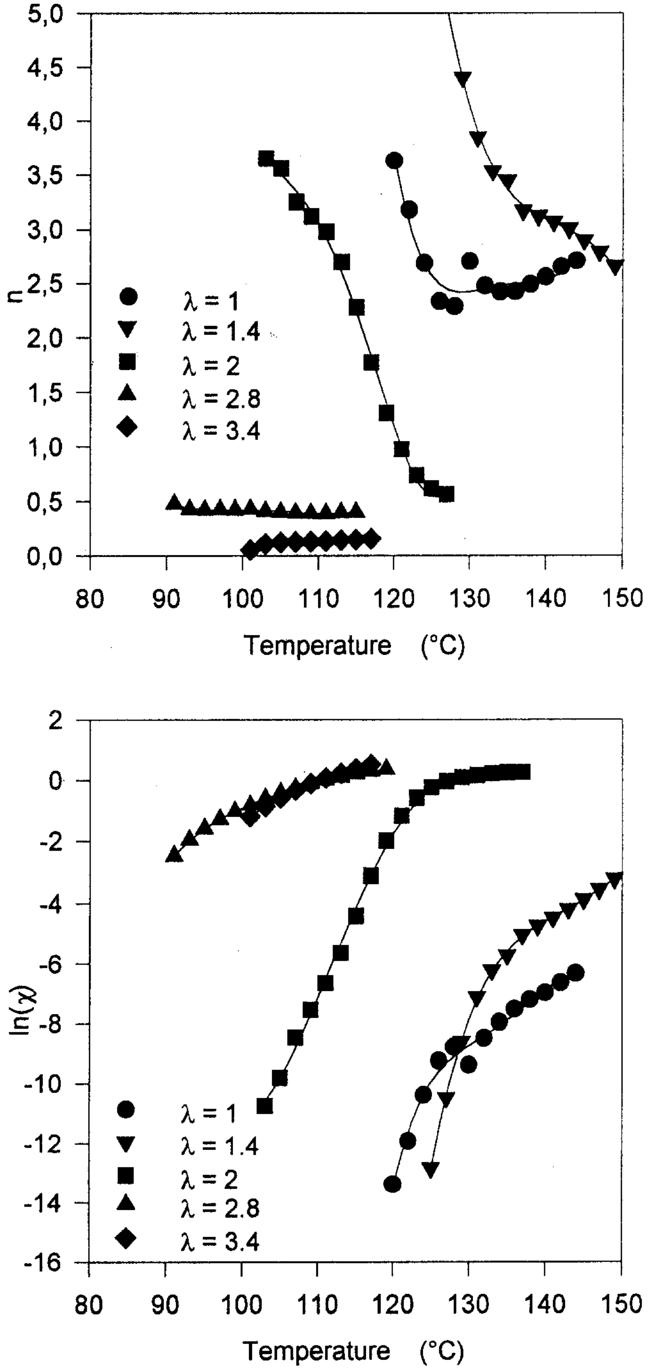

Fig. 6 Variation of the (a) Avrami exponent *n*; and (b) ln(χ) with the temperature for each draw ratio

$\lambda = 1$ and $\lambda = 1.4$ to a one-dimensional growth for $\lambda = 2.8$ and $\lambda = 3.4$. In this last case, heating leads to a growth of the initial oriented crystallines zones.

Conclusion

The drawing submitted to the PET films have clearly modified the thermal crystallization kinetics. The Ozawa's analysis shows: i) the disappearance of the spherulitic crystallization when the sample is strain induced crystallized; ii) the temperature independent growth of the initial oriented crystalline zones. Above $\lambda = 4$, the heating does not modify the crystalline state of the material (the apparent activation energy becomes infinite).

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