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Crystallization during hot-drawing of poly(ethylene terephthalate) film: influence of the deformation mode

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We have examined the influence of the strain-rate mode—constant extension rate (CER) and constant strain rate (CSR)—on crystallization kinetics during hot-drawing of poly(ethylene terephthalate) film. It was found that strain rate/draw time superposition, previously observed in CER drawing, is also applicable to CSR drawing, and that the temperature dependence of the shift factor is essentially the same in both modes of deformation. In CSR drawing, crystallization onset occurs at shorter times and the rate of crystallization is higher. Further analysis of the CSR data confirms previous CER data showing that at high strain rates the crystallization rate during drawing increases with temperature, and that this trend gradually reverses as strain rate decreases.

(Keywords: poly(ethylene terephthalate); strain rate; draw temperature)

Introduction

For drawing of amorphous, unoriented poly(ethylene terephthalate) (PET) film above the glass transition temperature, decreasing strain rate shifts the onset of crystallization to higher draw ratios and reduces the rate at which crystallinity increases with draw ratio[1–3]. This is because reducing strain rate increases the time available for orientational relaxation and, therefore, increases the draw ratio required to attain the critical orientation for crystallization[3,4].

We reported previously[5,6] that plots of crystallinity *versus* draw time at various strain rates $\dot{\varepsilon}$ can be shifted along the log time axis to superpose each other, and that the shift factor $A_{\dot{\varepsilon}}$ is given by:

$$A_{\dot{\varepsilon}} = C\dot{\varepsilon}^n \tag{1}$$

where n depends on draw temperature, and is related to the rate of molecular relaxation at the temperature. If the crystallinity *versus* draw ratio relationship were independent of strain rate, n would equal unity. The faster the relaxation, the greater is the delay in crystallization onset, and the more n exceeds unity.

In our experiments, the PET films were always stretched on an Instron tensile tester at a constant extension rate (CER). During this type of deformation the strain rate decreases continuously from its nominal value, such that:

$$\dot{\varepsilon} = (t + l_0/v)^{-1} \tag{2}$$

where t is draw time, l_0 is the original specimen length and v is the extension rate. This type of deformation is sometimes used in the industrial manufacture of PET film (tenter drawing).

It is also possible to draw at a constant strain rate (CSR). In this case the extension rate (or jaw speed) is continuously adjusted to maintain a constant rate of strain. The relationship between draw ratio λ and draw time t is then given by:

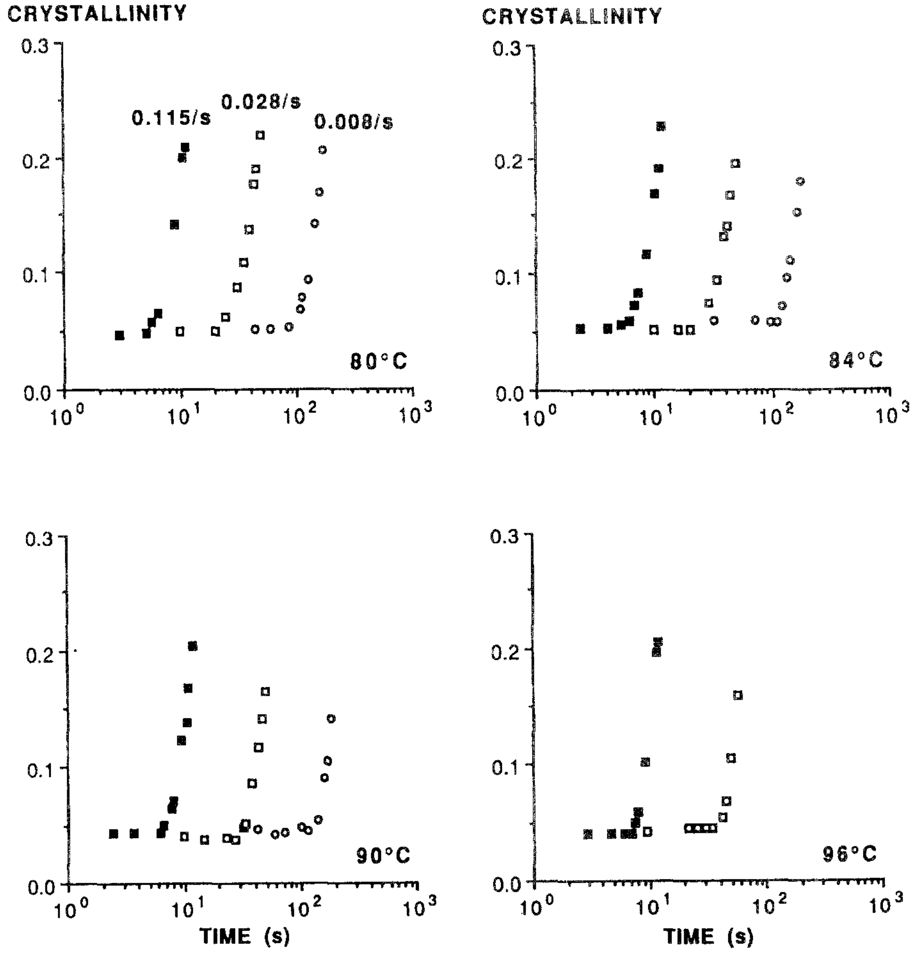
$$\lambda = \exp(\dot{\varepsilon}t) \tag{3}$$

Experimental studies of crystallization during CSR drawing of PET have been reported by Le Bourvellec *et al.*[2,3]. Since they examined the development of crystallinity as a function of draw ratio at various strain rates and draw temperatures, their data can be used to determine whether strain rate/draw time superposition is applicable to CSR deformation and to what extent the crystallization kinetics are influenced by the strain rate history. The PET film used by Le Bourvellec *et al.* (supplied by Rhône-Poulenc) had a number average molecular weight of about 20 000, and is therefore comparable to the Goodyear film with $\bar{M}_n = 21\,000$ used in our study[6]. Both the Goodyear and the Rhône-Poulenc films were clear and free of additives.

Analysis

From the CER data, two crystallization regimes were identified[1,6]: a low stress regime in which crystallinity increases relatively fast (regime 1), and a high stress regime in which crystallinity increases slowly (regime 2). In the CSR data, however, regime 2 crystallization is not evident[2], probably because the draw ratios used were not high enough to reveal it. In the present analysis, we therefore focus on regime 1 kinetics.

We have plotted the crystallinity data of Le Bourvellec *et al.*[2] as a function of draw time at the four draw temperatures they investigated (*Figure 1*). For each temperature, the crystallinity–time curve at the lowest strain rate was arbitrarily chosen as the reference, and the curves of higher strain rate were shifted to superpose it. *Figure 2* shows the superposed data on a linear time scale for the four temperatures, and in *Figure 3*, $\log A_{\dot{\varepsilon}}$ is plotted against $\log \dot{\varepsilon}$. It is evident that strain rate/draw time superposition is indeed applicable to CSR drawing, and that $A_{\dot{\varepsilon}}$ and $\dot{\varepsilon}$ are related by a power law, as given in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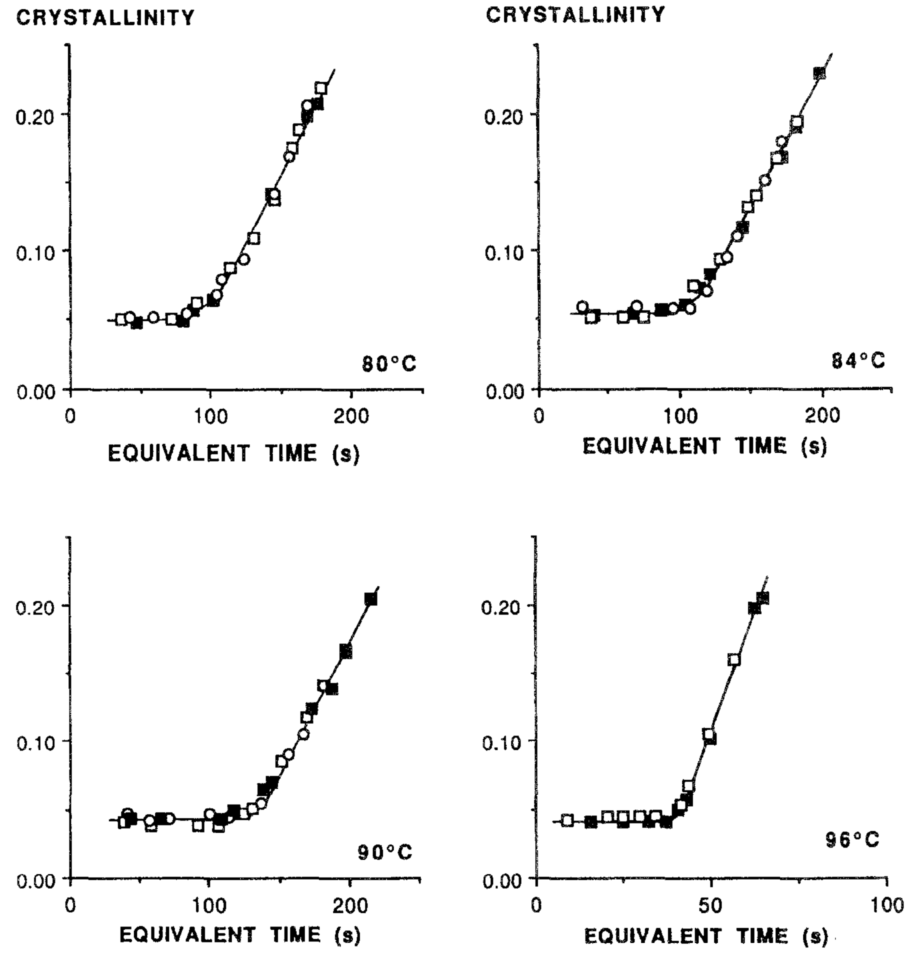
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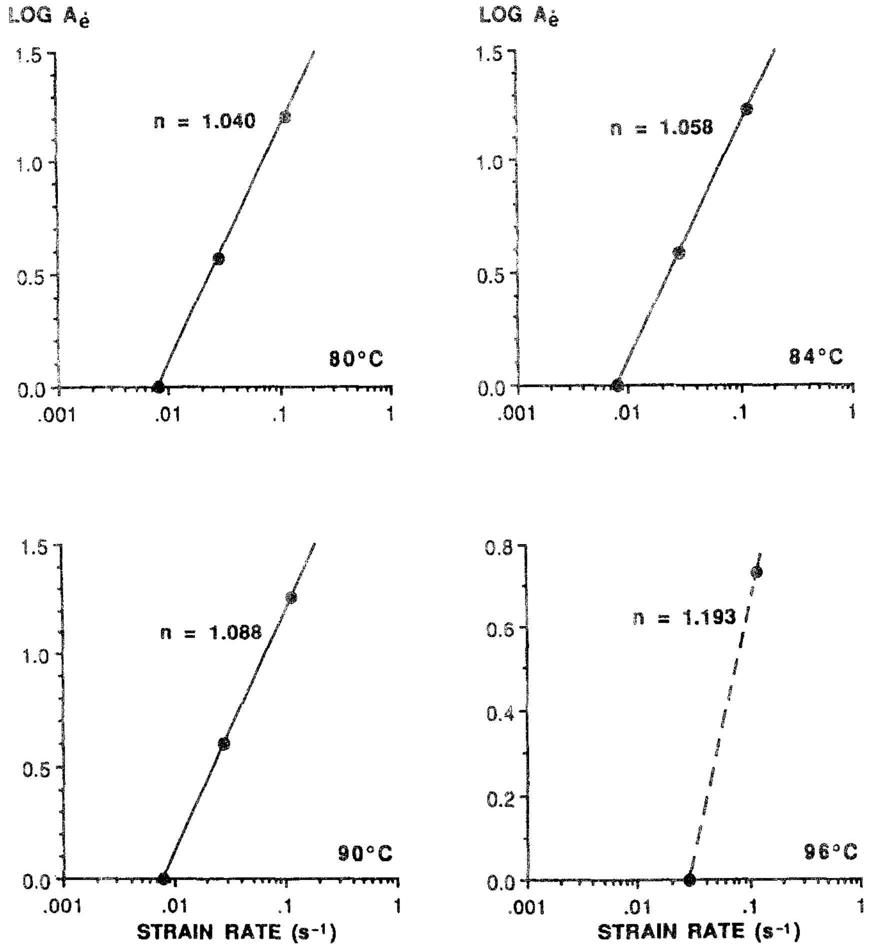

Figure 3 Relationship between shift factor $A_{\dot\varepsilon}$ and strain rate at various draw temperatures for CSR drawing

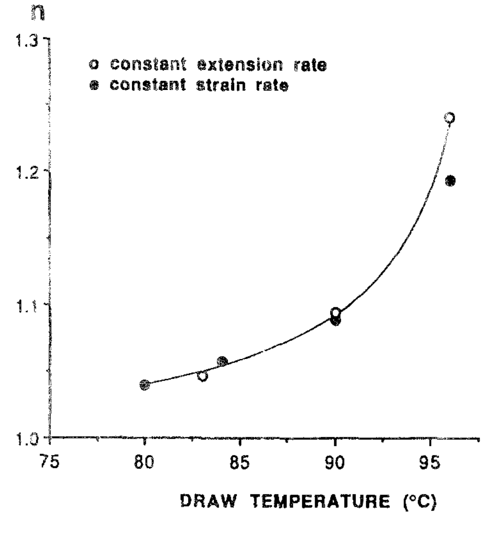

Figure 4 Dependence of n on draw temperature for CER drawing and CSR drawing

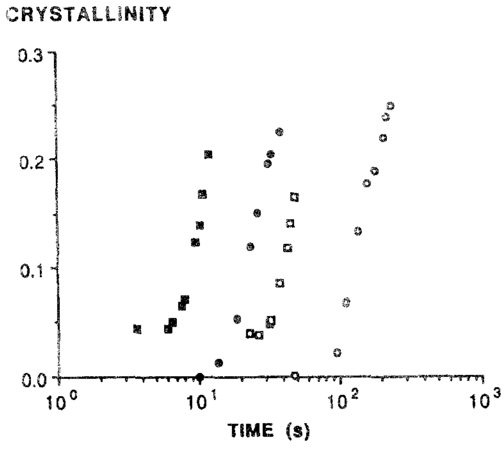

Figure 5 Crystallinity *versus* draw time at 90°C for CSR drawing at $0.28\,s^{-1}$ (■) and $0.008\,s^{-1}$ (□), and for CER drawing at nominal strain rates of $0.21\,s^{-1}$ (●) and $0.01\,s^{-1}$ (○). The strain rates in the two modes of deformation are close enough to permit rough comparison

Figure 1 (Top, left) Crystallinity *versus* draw time at various strain rates and draw temperatures for CSR drawing (obtained from the crystallinity *versus* draw ratio data of Le Bourvellec *et al.*[2])

Figure 2 (Bottom, left) Superposition of the data in *Figure 1*. The reference strain rate is $0.028\,s^{-1}$ at 96°C and $0.008\,s^{-1}$ at the other temperatures

equation (1). Moreover, *Figure 4* shows that the temperature dependence of n is essentially the same for CSR and CER drawing. The only significant discrepancy is at 96°C, which may arise from the fact that the n value at constant strain rate was obtained from only two strain rates (see *Figure 3*) and is therefore less accurate than the constant extension rate value.

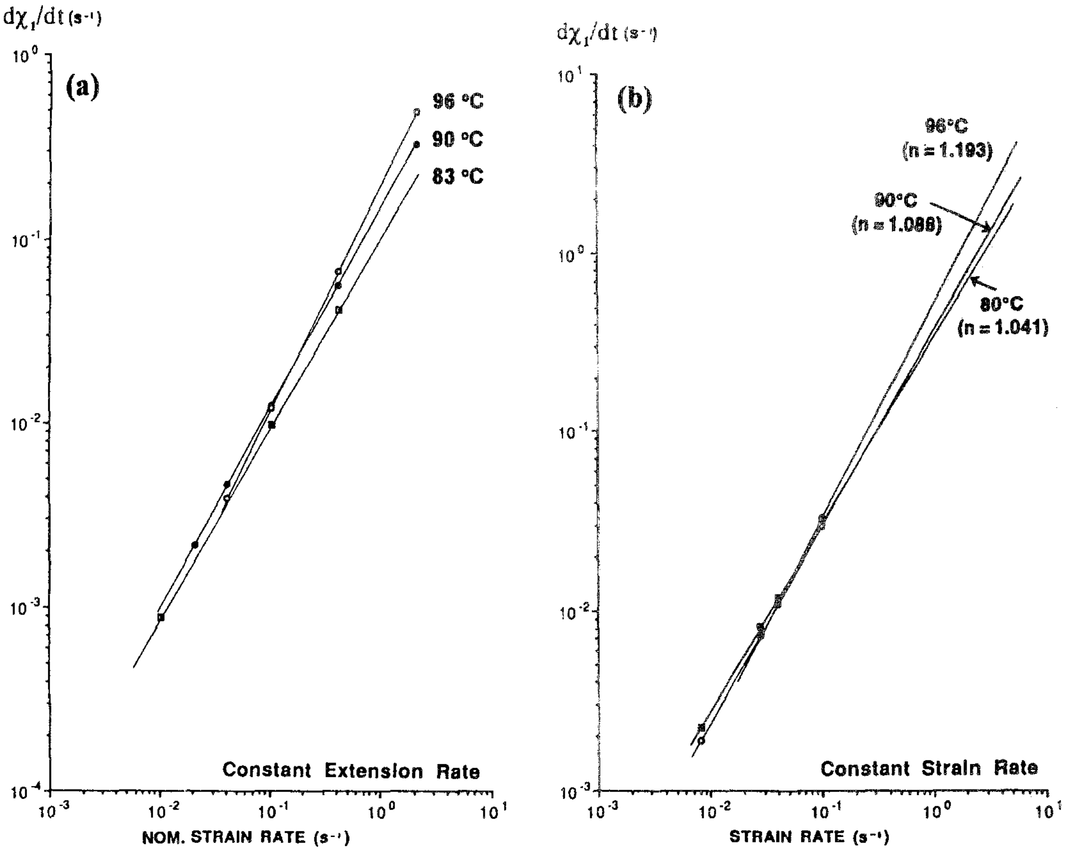

Figure 6 Crystallization rate in regime 1 as a function of (a) nominal strain rate for CER drawing, and (b) strain rate for CSR drawing

It seems that the effect of drawing at constant strain rate, rather than at constant extension rate, is to move the onset of crystallization to shorter times without altering the magnitude of the strain-rate dependent shift along the time axis (*Figure 5*). CSR drawing does result, however, in a higher rate of crystallization. For example, the crystallization rate at 90°C is $0.03\,s^{-1}$ at a constant strain rate of $0.1\,s^{-1}$, but at a nominal strain rate of $0.1\,s^{-1}$ in CER drawing it is only $0.01\,s^{-1}$ (in regime 1). This is because the rate at which crystallization is induced during drawing depends primarily on the rate at which molecular orientation is developed. Since strain rate decreases during CER drawing, the time available for orientational relaxation increases, resulting in slower crystallization kinetics.

As discussed previously[6], it follows from equation (1) that the crystallization rates in regimes 1 and 2 are given by:

$$d\chi_{1,2}/dt = K_{1,2}\dot{\varepsilon}^n \qquad (4)$$

This is demonstrated in *Figure 6* for CER and CSR drawing. Le Bourvellec *et al.* observed no influence of temperature on crystallization rate in CSR drawing[3]. *Figure 6b* demonstrates that within the strain rate range they studied (0.008–$0.1\,s^{-1}$) the influence of temperature is indeed negligibly small, but it also reveals that draw temperature would significantly influence crystallization rate at strain rates exceeding $0.1\,s^{-1}$. Temperature dependence of the crystallization kinetics is determined by two competing effects: higher temperatures enhance (1) the rate of orientational relaxation of uncrystallized chains, and (2) the rate of crystallization at a given level of 'amorphous orientation'. When strain rate is high, the latter temperature effect predominates because the time available for relaxation is very short, but as strain rate decreases, this effect is increasingly offset by the relaxation process. Thus the product:

$$(\delta\chi/\delta\langle P_2\rangle)_{t,T}(\delta\langle P_2\rangle/\delta t)_T$$

which largely controls the crystallization kinetics[3], is not in fact a constant at a given strain rate, and can only be approximated as such over a specific strain rate range.

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References

1 Salem, D. R. *Polymer* 1992, **33**, 3182
2 Le Bourvellec, G., Monnerie, L. and Jarry, J. P. *Polymer* 1986, **27**, 856
3 Le Bourvellec, G., Monnerie, L. and Jarry, J. P. *Polymer* 1987, **28**, 1712
4 Clauss, B. and Salem, D. R. *Polymer* 1992, **33**, 3193
5 Salem, D. R. *Polymer* 1992, **33**, 3189
6 Salem, D.R. *Polymer* 1994, **35**, 771