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A comparison of some models for describing polymer crystallization at low deformation rates

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Abstract

There is now in the literature a number of mathematical models of the effects of flow on crystallization of polymers, and here we compare the performance of various models in slow simple shearing and sinusoidal strain (oscillatory) flows. We compare the model predictions to the experiments of Wassner and Maier [E. Wassner, R.-D. Maier, Shear-induced crystallization of polypropylene melts. in: D.M. Binding, et al. (Ed.), Proceedings of the XIII International Congress on Rheology, Cambridge, 2000, pp. 1–183] on isotactic polypropylene. Both the Kolmogorov [A.N. Kolmogorov, On the statistics of the crystallization process on metals. Bull. Akad. Sci. USSR, Class Sci., Math. Nat. 1 (1937) 355–359] and Nakamura et al. [K. Nakamura, T. Watanabe, K. Katayama, T. Amano, Some aspects of non-isothermal crystallization of polymers I, J. Appl. Polym. Sci. 16 (1972) 1077–1091] crystallinity formulations are discussed, and the advantages of the former are emphasized. For the cases considered, we see that strain-based crystallinity enhancement formulations appear to give results close to the experiments at the low flow rates which were studied, although they have some drawbacks. Several other ideas also lead to acceptable results; a new formulation based on both strain and strain-rate appears to give the best overall fit.

Keywords: Flow crystallization; Slow shearing; Sinusoidal motion; Strain; Strain-rate

1. Introduction

The prediction of the impact of flow on crystallization, and the impact of crystallization on flow, are of great practical interest, and a considerable literature on the subject now exists. Reviews by Keller and Kolnaar [4], Eder et al. [5] and Eder and Janeschitz-Kriegl [6] are helpful. In the present paper, we shall mainly concentrate on shearing flows, and in this case several theories of crystallization enhancement by flow have been proposed. Eder and Janeschitz-Kriegl [6] discussed strain-rate driven enhancement; Keller and Kolnaar [4] proposed strain enhancement; Doufas et al. [7] discussed, in the context of melt-spinning, the effect of the trace of the stress tensor; Ziabicki et al. [8] suggested (in melt-spinning) that the normal stress difference (N_1) was important; Zheng and Kennedy [9] considered the change in dumbbell free energy induced by flow; Zuidema et al. [10] investigated a theory based on recoverable strain, and Janeschitz-Kriegl [11] suggested a work input criterion. This list does not contain every published paper, but we believe it does contain representatives of the main types of explanations on offer. Some arguments purport to relate molecular theories to 'macroscopic deformation'; here, we shall avoid such arguments and only consider macroscopic measurable parameters. From the above, we see that there does not seem to be a consensus of opinion on the cause of flow-induced crystallization.

There are also several viewpoints on the way crystallization affects rheology. Doufas et al. [7] consider that the stresses in the rigid (crystalline) phase plus the stresses in the amorphous phase simply add up; Tanner [12,13] has expressed doubts about this addition; he proposed a suspension-based theory whereby "rigid" crystals are embedded in an amorphous matrix, and showed that a more complex stress calculator was then essential. Zheng and Kennedy [9] and Ziabicki et al. [8] also used types of suspension theory. Here,

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we assume that the amorphous matrix properties are known; this is the simplest assumption. Further developments of the theory may need more complex assumptions (for example, gelling) but they are not considered here. In the present paper, where various theories will be compared, in the first instance, to the slow shear flows discussed by Wassner and Maier [1], we will adopt a simple suspension model of crystallizing rheology, to be detailed below. The advantage of using the Wassner–Maier experiments is that the complexity due to varying temperature is avoided; also, they deal with isotactic polypropylene (i-PP), which, as a common injection-moulding material, is well studied.

The aim of this paper is thus to apply all seven of the above-mentioned "causes" of enhanced crystallization to a simple rheological model and compare the results to the Wassner–Maier experiments.

2. Crystallization and flow

The basic equation of Kolmogorov [2] for the crystallinity fraction α is

$$\alpha = 1 - \exp(-\alpha_{\mathrm{f}}) \tag{1}$$

where

$$\alpha_{\mathrm{f}} = C_m \int_0^t \dot{N}(s)\left[\int_s^t G(u)\,\mathrm{d}u\right]^m \mathrm{d}s \tag{2}$$

Here, m is assumed to be a constant number denoting the dimensionality of the crystallites: in the original form for spherical crystals (Kolmogorov [2], Avrami [14]), $m = 3$, and the constant $C_m = 4\pi/3$. Generally, one finds $m = 1$–3, and it is not necessarily an integer.

$\dot{N}(t)$ is the rate of increase of number of nuclei in the crystallization process, and $G(t)$ is the linear rate of growth (distance/time) of the crystals.

We shall assume:

$$N = N_0 + N_{\mathrm{f}} \tag{3}$$

where N_0 is the number of existing nuclei at the beginning of the process ($t = 0$) and N_{f} is the number of nuclei created by the flow. N_0 is a function of temperature [6]. Monasse [15] has investigated crystal growth rates under shear in polyethylene. Growth rates vary linearly with shear rates in the range 0–4 s^{-1}; modest variations (~20% increase) arise for shear rates 0–0.5 s^{-1}, which is the range of interest here. Following this work and related investigations by Koscher and Fulchiron [16] we shall assume that G is a function of temperature only, and is not affected by the flow. However, it has been found by numerous workers (e.g. Eder and Janeschitz-Kriegl [6]) that $\dot{N}_{\mathrm{f}}$ is greatly affected by flow as well as temperature (and possibly pressure, here ignored).

We adopt the suggestion that [6,9]:

$$\dot{N}_{\mathrm{f}} + \frac{N_{\mathrm{f}}}{\lambda_{\mathrm{N}}} = g \tag{4}$$

where λ_{N} is a (large) temperature-dependent time constant and g usually depends on the flow variables, as well as the temperature. At a constant temperature and constant g ($=g_0$) one can solve (4) to find ($N_{\mathrm{f}} = 0$ at $t = 0$):

$$N_{\mathrm{f}} = \lambda_{\mathrm{N}} g_0 \left[1 - \exp\left(\frac{-t}{\lambda_{\mathrm{N}}}\right)\right] \tag{5}$$

If the flow halts, so g vanishes at t_1, say (and g was constant for $0 \leq t < t_1$, equal to g_0), then the solution of (4) shows that, for $t > t_1$:

$$N_{\mathrm{f}} = g_0 \lambda_{\mathrm{N}} \left(1 - \exp\left(\frac{-t_1}{\lambda_{\mathrm{N}}}\right)\right) \exp \frac{t_1 - t}{\lambda_{\mathrm{N}}}. \tag{6}$$

Hence, a slow collapse of N_{f} occurs for $t > t_1$, as observed. For the case where $t < t_1$, we have:

$$\dot{N}_{\mathrm{f}} = g_0 \exp\left(\frac{-t}{\lambda_{\mathrm{N}}}\right) \tag{7}$$

For small t/λ_{N}, $\dot{N}_{\mathrm{f}}$ is nearly equal to g.

The main task is to derive a form for g, in terms of flow variables, that is compatible with experiments. In general this is difficult, but by assuming isothermal flow and that $G = G_{\mathrm{T}} =$ constant [15] we find:

$$\alpha = 1 - \exp - \left[C_m G_{\mathrm{T}}^m \int_0^t \dot{N}(s)(t - s)^m \,\mathrm{d}s\right] \tag{8}$$

To include nuclei existing at $t = 0$ (N_0) we assume $N_0 = N_0 H(t)$, where $H(t)$ is a unit step function, and hence, (8) becomes:

$$\alpha = 1 - \exp - \left[K_0 t^m + K_{\mathrm{f}} \int_0^t \dot{N}_{\mathrm{f}}(t - s)^m \,\mathrm{d}s\right] \tag{9}$$

where $K_{\mathrm{f}} = C_m G_{\mathrm{T}}^m$ and $K_0 = N_0 K_{\mathrm{f}}$.

We can compare (9) with the Nakamura et al. [3] formulation, which was devised for quiescent variable temperature conditions; this formula is:

$$\alpha = 1 - \exp\left[\int_0^t K_{\mathrm{N}}\,\mathrm{d}t'\right]^n \tag{10}$$

where K_{N} is a function of temperature and the flow conditions. When K_{N} is constant the familiar $K_{\mathrm{N}}^n t^n$ form emerges. In differential form (10) is:

$$\frac{\mathrm{D}\alpha}{\mathrm{D}t} = n(1 - \alpha)[-\ln(1 - \alpha)]^{(n-1)/n} K_{\mathrm{N}} \tag{11}$$

This form, as emphasized by various writers (e.g. Eder and Janeschitz-Kriegl [6]), lacks the detailed physics and the flexibility of (2), even though (11) gives a convenient way to find K_{N} once n is known. In the quiescent case $n = m$.

It is sometimes useful to use the Schneider et al. [17] forms resulting from repeated differentiation of the square-bracketed term in Eq. (8). We have in the isothermal case, where $G = G_{\mathrm{T}} =$ constant:

$$\alpha_{\mathrm{f}} = C_m G_{\mathrm{T}}^m \int_0^t \dot{N}_t(s)(t - s)^m \,\mathrm{d}s \tag{12}$$