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Micro-Rheological Modeling of Flow-Induced Crystallization in Mixed Shear/Extensional Flows

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Summary: Flow Induced Crystallization (FIC) is the common term to indicate the acceleration in polymer crystallization kinetics due to the action of flow. When modeling FIC, two major challenges are encountered. On the one hand, the model must be able to produce quantitative reliable results, while correctly describing the coupling between the intrinsic (quiescent) crystallization kinetics and the rheological response of the polymer. On the other hand, the model must be able to describe the complex kinematics taking place in real industrial processes. In this paper, we present the predictions of a recently proposed model for FIC in the case of a mixed flow, where both shear and extensional components are present at the same time. In particular, the effects of the overall flow intensity and of relative weight between shear and extension on the enhancement in nucleation rate are presented and discussed. Some guidelines for future development are also proposed.

Keywords: crystallization; rheology

Introduction

Flow Induced Crystallization (FIC) is the general term to indicate the effects that flow has on both the rate of crystallization and the morphology of a thermoplastic polymer[1]. One major feature of FIC is the enhancement of the polymer crystallization rate with respect to quiescent conditions. When subjected to flow, the polymer chains are oriented and possibly stretched. The resulting entropy decrease (or the equivalent free energy increase) makes crystallization more favorable, at least in the nucleation stages[2,3], thus generating an acceleration in crystallization kinetics.

Flow-induced crystallization is particularly relevant in those processes where high velocity gradients are reached, such as high-speed fiber spinning and injection molding. In the former, a purely extensional flow is applied to the polymer melt during cooling. The high orientation imparted to the polymer chains is responsible for a strong enhancement of the crystallization rate[4,5]. In the latter, the situation is much more complex. In some regions, such as thin, slit-like sections, high shear rates dominate. In others, mixed shear/extension kinematics are

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present. In both cases flow is found to strongly affect the resulting crystalline microstructure[6-8].

Modeling the interactions between flow and crystallization still remains at a relatively primitive stage. Several phenomenological models have been proposed to predict the influence of flow on crystallization kinetics[9-12]. A major advantage of these models is the possibility to apply them to actual process conditions. A price to be paid, however, is the determination of several adjustable parameters.

In the last two decades, increasing attention has been paid to micro-rheological modeling of the FIC. Within this framework, dumbbell-like models have been initially used to calculate a flow-induced change in the free energy of the amorphous phase, and the subsequent crystallization rate enhancement[13]. Although such models are able to qualitatively predict the effects of flow on crystallization, their quantitative performance is poor, as the rate enhancement is predicted to be several orders of magnitude larger than that observed experimentally. This fact should not be surprising, as dumbbell models fail in correctly predicting the rheological response of polymer melts.

Very recently[14-16] our group has proposed a new micro-rheological crystallization model, which is based on the Doi-Edwards (DE) theory. The DE model is known to successfully describe most of the rheological features of high molecular weight, linear polymer melts[17]. The model was used to predict quantitatively several experimental results of flow-induced crystallization under isothermal, steady-state, low shear rate conditions.

In this paper we extend the model to the case of a complex flow, namely, a mixed shear/extension flow field. The chosen flow condition enjoys two different peculiarities. On the one hand, as it will be shown in the next section, it can be easily obtained in the classical four-roll-mill geometry, a laboratory scale configuration which has been used by several experimental investigators to study the behaviour of polymer fluids under complex flow conditions[18-20]. On the other hand, it represents the prototype of those complex flow conditions experienced in real industrial processes that are the final objective of any predictive model for flow-induced crystallization.

The paper is structured as follows. After this introduction, the basic features of the model are described, and the mixed shear/extension flow field conditions are implemented into the basic equations of the model. Next, the predictions of the model are shown, and the effects of the flow parameters (the total intensity of flow and the relative intensity of shear and extension) are discussed. The paper is closed by some final remarks.

The model

In this section, the main features of the proposed model are described. Further details can be found elsewhere[14]. The starting point of the model is the well known expression for the isothermal nucleation kinetics as proposed by Lauritzen and Hoffman [21]:

$$\dot{N} = CkT\Delta G \exp\left(-\frac{E_a}{kT}\right)\exp\left[-\frac{K}{T(\Delta G)^n}\right] \qquad (1)$$

In Eq. (1), C contains constant factors which are not relevant for the present discussion, k is the Boltzmann constant, T the absolute temperature, E_a is the activation energy for the jump rate of the chain segment at the supercooled liquid-nucleus interface and K is a constant containing energetic and geometrical factors of the crystalline nucleus. The exponent n accounts for the temperature region where the homogeneous nucleation takes place, and can generally assume the values 1 and 2[9]. $\Delta G = G_L - G_S$ is the volumetric free energy difference between liquid and crystalline phase that, to a good approximation, can be expressed as:

$$\Delta G = \Delta G_q = \Delta H_0\left(1 - \frac{T}{T_m}\right) \qquad (2)$$

where T_m is the thermodynamic crystallization temperature.

We now assume that flow contributes additively to the free energy of the melt phase. As a consequence, the free energy difference can be written as:

$$\Delta G = \Delta G_q + \Delta G_f \qquad (3)$$

where ΔG_q refers to quiescent conditions, and ΔG_f is the contribution due to the action of flow.

The effect of flow on crystallization can be evaluated by considering the ratio, Ψ, of the flow-induced nucleation rate with respect to its quiescent value. Using Eqs. (1) and (3), Ψ can expressed as:

$$\Psi \equiv \frac{\dot{N}_f}{\dot{N}_q} = \left(1 + \frac{\Delta G_f}{\Delta G_q}\right)\exp\left[\frac{K}{T(\Delta G_q)^n}\left(1 - \frac{1}{(1 + \Delta G_f/\Delta G_q)^n}\right)\right] \qquad (4)$$

Obviously, this dimensionless nucleation rate is unity under quiescent conditions, whereas $\Psi>1$ when flow is applied.

The main assumption in this model is that rheological properties are not significantly affected by the presence of nuclei. This assumption is expected to be reasonable at least in the early stages of crystallization. The flow-induced free energy change is then calculated by using the Doi-Edwards (DE) micro-rheological model for the pure melt, in the so-called Independent Alignment Approximation version:

$$\Delta G_f = \frac{3\rho N\ kT}{M_e} \int_{-\infty}^{t} \mu(t,t')\, A\left[\mathbf{E}(t,t')\right] dt' \qquad (5)$$

In Eq. (5), ρ is the melt density, N the Avogadro number, and M_e the molecular weight between entanglements. μ is the DE memory function:

$$\mu(t,t') = \frac{8}{\pi^2} \sum_{p\ odd} \frac{1}{p^2} \exp\left[-\frac{p^2(t-t')}{T_d}\right] \qquad (6)$$

where T_d is the disengagement time. The function $A[\mathbf{E}(t,t')]$ is given by:

$$A\left[\mathbf{E}(t,t')\right] = \left\langle \ln\left[\left|\mathbf{E}(t,t')\cdot\mathbf{u}\right|\right]\right\rangle_0 \qquad (7)$$

where $\mathbf{E}(t,t')$ is the deformation history tensor between times t' and t, $\mathbf{u}$ is the unit pseudo-vector associated to a primitive chain segment, and the symbol $\langle\cdot\rangle_0$ indicates the average over the orientational equilibrium distribution function[17,22].

Once the flow kinematics are assigned (through the tensor $\mathbf{E}$) the free energy flow term is computed from Eq.(5). This allows for the calculation of the effect of flow on the nucleation rate by means of Eq. (4). It should be noticed here that the set of Equations (4)-(7) contains no adjustable parameters. All physical quantities appearing in these equations can be in principle determined from independent measurements[14].

As said in the Introduction, the above model has been successfully used to predict the enhancement in nucleation rate under isothermal steady shear flow. One example is given in Figure 1, showing the good agreement between model predictions and experimental data for an isotactic polypropylene[15].

The results reported in Figure 1 refer to simple shear flow, that is, to flow conditions which do not realistically represent those encountered in real processes. For this reason, the model is here extended to the case of a complex flow, i.e., where both shear and extensional components are simultaneously present.

In the present case the flow kinematics are represented by the following two-dimensional velocity gradient tensor **K**:

$$\mathbf{K} = \frac{1}{2}\dot{\xi}\begin{bmatrix} 1+\alpha & 1-\alpha \\ -(1-\alpha) & -(1+\alpha) \end{bmatrix} \tag{8}$$

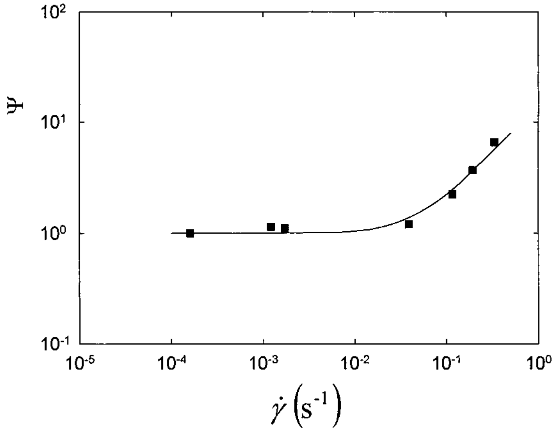

Figure 1. The dimensionless nucleation rate as a function of shear rate for an isotactic polypropylene at 140°C[15]. Points are experimental data. The solid line is the prediction of the model.

Tensor **K** is a well known example of a mixed shear/extensional flow field. In particular, it represents the flow field developing at the stagnation point of a four roll mill apparatus[18]. The geometry of the four roll mill is schematically reported in Figure 2, along with the coordinate reference system used to generate the component form of **K** reported in Eq.(8).

Two parameters appear in Eq.(8). $\dot{\xi}$ is the magnitude of the flow field, α is a flow parameter accounting for the relative strength between the extensional and the shear component in the flow. In particular, when α=1 a purely planar extensional flow is obtained. Conversely, when α=0, pure shear flow is attained. Varying α between these limits allows for the application of a mixed shear/extension flow field to the polymer at the stagnation point. In a four roll mill apparatus the value of α can be changed at will by suitably adjusting the angular velocity of the four rolls[18].

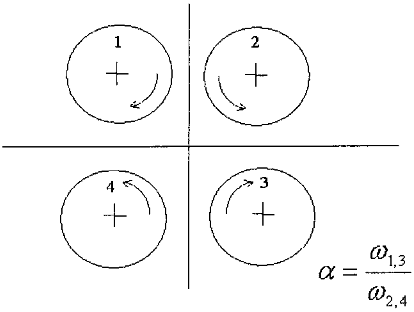

Figure 2. The geometry of the four roll mill. The definition of the flow parameter α and the two axes used to represent the velocity gradient tensor of Eq. (8) are also reported.

Once the flow kinematics are assigned through tensor **K**, the crystallization model can be implemented if the deformation history tensor is known. If steady-state conditions are assumed, **E** can be derived from the velocity gradient tensor by using the general relationship[22]:

$$\mathbf{E}(t,t') = \exp\left[\mathbf{K}(t-t')\right] \qquad (9)$$

The full expression of **E** is then given by:

$$\mathbf{E}(z) = \begin{bmatrix} \cosh\left(zDe\sqrt{\alpha}\right) + \dfrac{(1+\alpha)\sinh\left(zDe\sqrt{\alpha}\right)}{2\sqrt{\alpha}} & -\dfrac{(\alpha-1)\sinh\left(zDe\sqrt{\alpha}\right)}{2\sqrt{\alpha}} \\ \dfrac{(\alpha-1)\sinh\left(zDe\sqrt{\alpha}\right)}{2\sqrt{\alpha}} & \cosh\left(zDe\sqrt{\alpha}\right) - \dfrac{(1+\alpha)\sinh\left(zDe\sqrt{\alpha}\right)}{2\sqrt{\alpha}} \end{bmatrix} \qquad (10)$$

where $z=(t-t')/T_d$, and $De=\dot{\xi}\,T_d$ is the Deborah number for this type of flow.

The deformation tensor can be inserted into Eq. (5) to determine the flow-induced free energy and, therefore, the dimensionless nucleation rate. The actual calculation has been carried out by using the commercial software Mathematica® on a personal computer. Numerical predictions are presented in next section.

Results and discussion

In order to obtain quantitative predictions from the model, the non-adjustable parameters appearing in the equations presented in the previous section must be set. In particular, as shown by Eqs (2), (4) and (5), the following parameters need to be specified: the constant K, accounting for the temperature sensitivity of the quiescent crystallization rate, and the corresponding exponent n; the thermodynamic crystallization temperature, T_m, and the corresponding heat of fusion, H_0; the polymer density, ρ, and the molecular weight between entanglements, M_e. The disengagement time, T_d, also appearing in the model equations, is not necessary in this case because all results will be given in terms of the dimensionless Deborah number that was defined above. As a way of an example, we choose the set of parameters relative to the isotactic polypropylene referred to in Fig.1. The parameters are summarized in Table 1. The melting temperature T_m and the crystallization kinetics constant K have been obtained from DSC measurements[23]. All other parameters are extracted from literature[24-26].The results presented below simulate the flow-induced crystallization at a temperature of 140°C.

Table 1. Experimental parameters for the isotactic polypropylene of Figure 1

H_0 [j/m^3]	T_m [K]	N	K [K(j/m^3)^n]	ρ [kg/m^3]	M_e [g/mol]
1.4×10^8	467	1	9.0×10^{10}	970	4623

Figure 3 shows the dimensionless free energy $\Gamma = \Delta G_f / \frac{3\rho N\ kT}{M_e}$ as a function of the Deborah number, and for different values of the flow parameter α. As expected, an increase of flow intensity determines a corresponding increase in the flow-induced free energy of the melt phase. It is also confirmed that, at a given flow rate, the extensional flow is more effective than shear in orienting the polymer chain. Also reported in Fig.3 is the free energy determined by a uniaxial extensional flow. The curve practically coincides to that for α=1 in the high De region. For low De, however, planar extension gives a substantially higher increase in free energy. This demonstrates that these two types of elongational flows determine different quantitative effects in terms of crystallization enhancement.

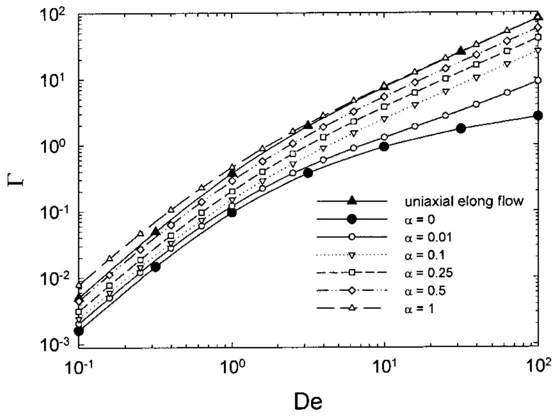

Figure 3. The dimensionless flow-induced free energy as a function of shear rate for different values of the flow parameter α.

Figure 3 also shows that the addition of an even small amount of elongation to a shear flow can produce dramatic effects in terms of free energy. This can be seen at high *De* when α=0.01. The direct effect of the complex flow on the crystallization rate is reported in Figs 4 and 5, where the dimensionless nucleation rate is plotted as a function of the Deborah number and of the shear/extension flow parameter.

In Fig.4 the effect of the flow magnitude is shown. Obviously the nucleation rate increases as the flow intensity increases. The great difference between shear and extensional flow is also very clear. The former, for the range of *De* explored, produces a maximum change in crystallization rate of about two decades. For the latter, the enhancement can be as high as six orders of magnitude at *De*=100. The relative importance of the extensional flow is also apparent when considering the effect of the flow parameter, α. It can be noticed that even for small values of α the nucleation rate is much higher than that determined under pure shear flow conditions. For example, for α=0.01 and *De*=100, Ψ is seen to increase by a factor of about 15 with respect to α=0.

The role of the relative weight of extension and shear on crystallization is further clarified in Fig. 5, where Ψ is plotted as a function of the flow parameter α. At low *De* the enhancement in crystallization rate is obviously small, but also no appreciable difference between shear and extension can be observed. On the contrary, at high *De* the increase in nucleation rate becomes relevant under any flow condition. The presence of even a small amount of extensional component, however, determines an abrupt upturn in flow-induced crystallization. Notice, for example, that for De=100 a value of α=0.2 determines already a "saturation" in the crystallization rate enhancement due to flow.

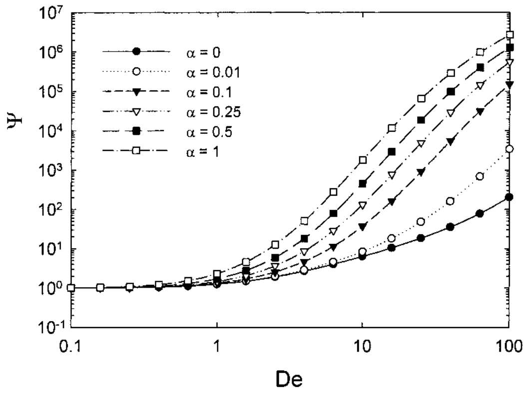

Figure 4. The dimensionless nucleation rate as a function of the Deborah number for different values of the flow parameter α.

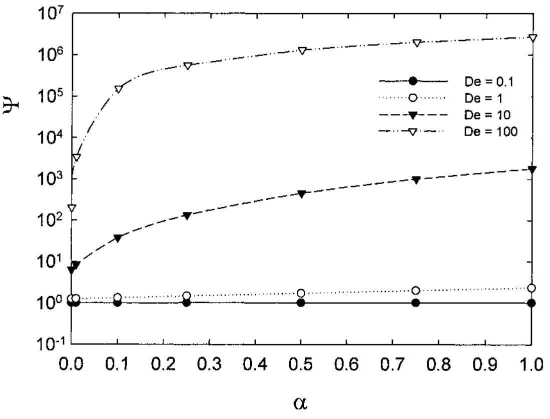

Figure 5. The dimensionless nucleation rate as a function of the flow parameter α for different values of the Deborah number.

Concluding remarks

The micro-rheological model already used elsewhere[14,16] to successfully describe the case of simple shear, is here proposed for a more complex flow situation, where both shear and extensional components are present. The results of the numerical calculations show that the model is able to provide quantitative results on the enhancement in crystallization rate and on the role of the two flow components at a relatively small mathematical and computational cost. Such results call for intensive future work along at least two different directions. On the one hand, the type of flow chosen for the calculations can be experimentally reproduced in a four roll mills apparatus. This would allow for a comparison between experiments and numerical calculations, and therefore for a more robust validation of the model, which has been so far tested only against simple, low shear rate experimental conditions. On the other hand, the model equations can in principle describe any type of flow kinematics, both under steady-state or transient conditions. Therefore, they can be inserted into numerical codes for the simulation of flow-induced crystallization under real, industrial processing conditions.

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