Coupling Between Kinetics and Rheological Parameters in the Flow-Induced Crystallization of Thermoplastic Polymers

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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. FIC is expected to be the result of the coupling between the intrinsic (quiescent) crystallization kinetics and the rheological response of the polymer. The choice of a suitable rheological model, therefore, is a crucial requirement for a successful FIC model. Recent work of our group[1] has demonstrated that the Doi-Edwards rheological model (DE), based on the concept of chain reptation, can be easily incorporated into classical crystallization models to successful predict the enhancement in nucleation rate under the action of a steady shear flow. In this paper, the interaction between the rheological parameters of the DE model and the crystallization kinetics parameters is investigated in more details. In particular, the effect of the crystallization temperature, which acts on both the polymer relaxation time and the free energy jump between liquid and solid phase, is determined and discussed.

Introduction

The enhancement of polymer crystallization rate under the action of flow, known as Flow Induced Crystallization (FIC), is a complex phenomenon that takes place in many common processing applications. The basic physics behind FIC, however, is relatively simple. 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 its nucleation stage[2,3], thus generating the observed acceleration in crystallization kinetics. Based on the above picture, intuition would suggest several "rules of thumb" for FIC. For example, it is obvious that extensional flows are more effective than shear-dominated flows in determining FIC[4]. Likewise, it is expected that longer chains, which are more effectively oriented than

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shorter ones under the same velocity gradient conditions, will determine a larger increase in nucleation rate[5].

In spite of the relative simplicity of the underlying physics, modeling of the FIC process turns out to be a formidable task, even when the very basic problem of isothermal crystalline nucleation under flow is addressed. Based on the above concepts, several modeling approaches to such a problem have been proposed in the literature. Empirical models directly relate the rate of crystallization enhancement to some measure of the flow intensity, such as the square of the shear rate or the total energy that flow transmits to the polymer[6]. Both the functional form of such models and the value of its adjustable parameters, however, rely on the comparison with experimental data, making them not at all predictive.

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[7]. Although such models are able to qualitatively predict the effects of flow on crystallization, their quantitative performance is very 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[1] 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[8]. The proposed model was able to predict quantitatively several experimental results of the flow-induced crystallization rate available in the literature. Two important properties of the model must be stressed. On the one hand, the model does not contain in principle any adjustable parameter. On the other hand, all the model parameters have a robust physical meaning. For this reason, a parametric study of the model behaviour appears to be useful to explore the effect of the various physical variables on flow-induced crystallization.

The model

In the proposed model the isothermal nucleation kinetics is expressed in terms of the Lauritzen and Hoffman theory[9]:

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

In Eq. (1), C contains factors which are not relevant for the present discussion, k is the Boltzmann constant, T the absolute temperature, $\Delta G = G_L - G_S$ the volumetric free energy difference between liquid and crystalline phase. E_a is an activation energy of 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].

Following a commonly accepted approach, it is assumed that the flow contributes additively to the free energy of the melt phase. Under this assumption, the free energy difference appearing in Eq. (1) can be written as:

$$\Delta G = \Delta G_q + \Delta G_f \tag{2}$$

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

In order to evaluate the effect of flow on crystallization, a characteristic time for the onset of crystallization is often measured[10,11]. Such a quantity, usually referred to as an "induction time", is roughly proportional to the inverse of the nucleation rate. Using Eqs. (1) and (2), the ratio Θ between the induction time under quiescent conditions and that under flow can be defined as:

$$\Theta \equiv \frac{\dot{N}_q}{\dot{N}_f} = \frac{1}{1+\Delta G_f/\Delta G_q}\exp\left[\frac{K}{T(\Delta G_q)^n}\left(\frac{1}{(1+\Delta G_f/\Delta G_q)^n} - 1\right)\right] \tag{3}$$

where the subscripts q and f refer to quiescent and flow conditions, respectively. Obviously, the dimensionless induction time is unity under quiescent conditions, whereas $\Theta<1$ when flow is applied.

Coppola *et al*[1] recently proposed the use of the Doi-Edwards (DE) reptation theory to determine ΔG_f. In fact, under the so-called Independent Alignment Approximation (IAA) the original DE model yields the following expression for ΔG_f[12]:

$$\Delta G_f = 3ckT \int_{-\infty}^{t} \mu(t,t') A\left[\mathbf{E}(t,t')\right] dt' \tag{4}$$

In Eq. (4), c is the volumetric concentration of primitive chain segments, μ is the DE memory function:

$$\mu(t,t') = \frac{8}{\pi^2} \sum_{p\ odd} \frac{1}{p^2} \exp\left[-\frac{p^2 (t-t')}{T_d} \right] \tag{5}$$

where T_d is the disengagement or reptation time, and $A[\mathbf{E}(t,t')]$ is given by:

$$A\left[\mathbf{E}(t,t')\right] = \left\langle \ln\left[\left| \mathbf{E}(t,t') \cdot \mathbf{u} \right| \right] \right\rangle_0 \tag{6}$$

In Eq. (6) $\mathbf{E}(t,t')$ 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[12].

The chain segment concentration is equivalent to an entanglement density and can be expressed as:

$$c = \frac{\rho N}{M_e} \tag{7}$$

where ρ is the melt density, N the Avogadro number, and M_e the molecular weight between entanglements.

For steady-state shear flow, Eq. (4) can be formally expressed as:

$$\Delta G_f = 3ckT\,\Gamma(De) \tag{8}$$

where $De = \dot{\gamma} T_d$ is the Deborah number, i.e., the product between the shear rate and the polymer reptation time, and Γ is a dimensionless free energy which is a function of *De* only and whose analytical details can be found in [12].

In order to evaluate Θ for a given polymer under isothermal shear flow conditions, several material parameters are needed. The quiescent free energy requires the knowledge of the thermodynamic melting temperature, T_{m}, and of the latent heat of fusion, H_0:

$$\Delta G_q = H_0 \left(1 - \frac{T}{T_{\mathrm{m}}}\right) \tag{9}$$

Further quiescent crystallization parameters are the constant K and the exponent n appearing in Eq. (3). In addition, rheological parameters of the polymer melts are required, namely, the reptation time, T_{d}, the melt density, ρ, and the molecular weight between entanglements, M_{e}.

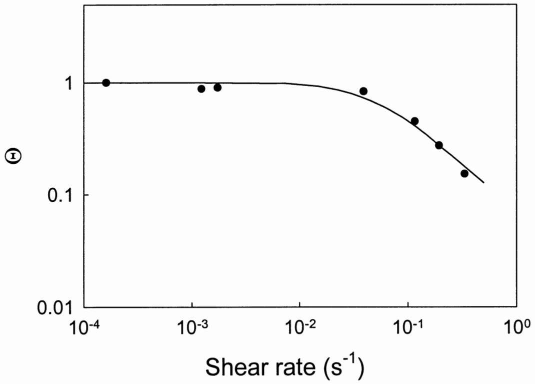

Figure 1. Dimensionless induction time as a function of shear rate for an isotactic polypropylene at 140°C. Points are experimental data. The solid line is the prediction of the model with T_{d}=40s (see text).

It must be stressed that all the above parameters can be in principle measured by independent experiments, thus making the model fully predictive. In practice, good agreement between model prediction and several experimental induction time data has been already demonstrated[1] when the reptation time is used as the only fitting parameter. One example is reported in Figure 1, where the dimensionless induction time as a function of shear rate is plotted for an isotactic polypropylene (iPP) at 140°C. The significant parameters are reported in table 1. The melting temperature T_m and the crystallization kinetics constant K have been obtained from DSC measurements[13]. All other parameters are extracted from literature[10,11,14].

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

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

Induction times were measured by detecting the sharp upturn in the viscosity vs. time curve under constant shear rate. Experiments were carried out in a DSR 200 Rheometric apparatus equipped with cone and plate fixtures (plate diameter 25mm, cone angle 0.017 rad). A typical viscosity vs. time plot, used to determine the induction time, is shown in Figure 2. The viscosity of the crystallizing polymer has been normalized with respect to its initial value. Notice the strong acceleration in crystallization kinetics when the shear rate is changed by one order of magnitude. At low shear rates the induction time is found to become shear rate independent. This value is assumed to be the quiescent induction time.

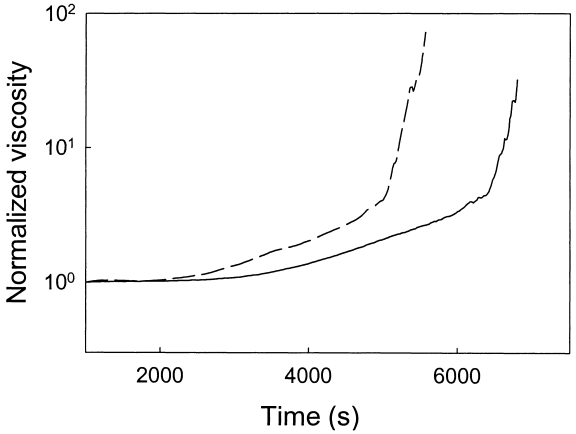

Figure 2. The normalized viscosity of isotactic polypropylene at 140°C as a function of the crystallization time for different shear rates. Solid line: 1.75×10^{-3} s^{-1}. Dashed line: 2.58×10^{-2} s^{-1}.

Temperature effects

In view of the promising agreement between model and experimental evidence, the predictive capabilities of the model are further investigated. In particular, the effect of temperature on the predicted induction time will be presented in this section.

A closer inspection of Eq. (3) shows that the crystallization temperature affects the model predictions in different ways. Apart from the explicit dependence appearing in Eq. (3), temperature is hidden in both ΔG_q and ΔG_f as apparent from Eqs. (8) and (9). In particular, the reptation time embedded in the Deborah number, representing a characteristic relaxation time of the polymer melt, obviously depends upon temperature[15]. As a consequence, the dimensionless induction time is a non trivial function of temperature. In order to clarify this point, calculations have been carried out for the same iPP referred to in Figure 1 also at temperatures different from that used in the experiments. The dependence of T_d on temperature has been extracted from time-temperature superposition of linear viscoelasticity data, whose results are presented in Figure 3 in terms of the shift factor a_T relative to the temperature of 230°C.

Linear regression of the data in Figure 3 provides the following equation for a_T:

$$a_T = 10^{\left(-4.4+\frac{2220}{T}\right)} \qquad (10)$$

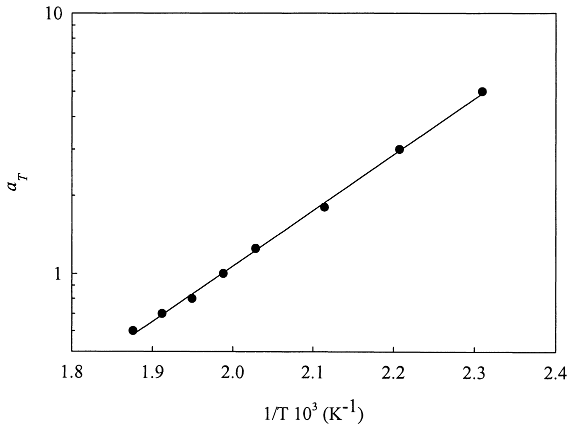

Figure 3. The shift factor for iPP from linear viscoelastic data. The reference temperature is 230°C.

From Eq. (10) the reptation time at any temperature can be calculated by using the value already estimated at 140°C (see Figure 1).

The results of the calculations are shown in Figure 4, where Θ is plotted as a function of the dimensional shear rate for three different temperatures. As the temperature approaches T_m, the effect of flow on the acceleration of the nucleation kinetics increases dramatically. This can be physically understood by considering that both ΔG_q and ΔG_f decrease as temperature increases, but in a completely different fashion. In fact, ΔG_q becomes vanishingly small as T approaches T_m, whereas ΔG_f is always non zero for any applied shear rate, due to the orienting action of the flow. As a consequence, the ratio $\Delta G_f/\Delta G_q$ becomes the controlling term in Eq. (3), thus generating the diverging effect displayed in Figure 4. It should be added that within the temperature window explored, which is of the order of a few tens of degrees, the magnitude of the polymer relaxation time does not change significantly, thus producing a relatively weak change of the ΔG_f term.

As a final remark, and in order to avoid any misleading conclusion, it must be stressed here that the predictions of Figure 4 refer to the *dimensionless* induction time, i.e., the ratio between a nucleation characteristic time under flow and the same time determined under quiescent conditions. Obviously, as the temperature approaches the nominal melting point, the *absolute* nucleation time always increases, but the *relative* effect of flow becomes larger and larger.

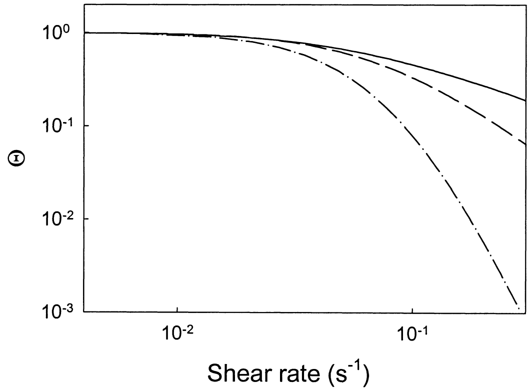

Figure 4. The effect of temperature on the dimensionless induction time for the iPP. Solid line: T=140°C; dashed line: T=160°C; dot-dashed line: T=177°C

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