Flow-induced crystallization of polymer: theory and experiments

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ABSTRACT: In this work we analyze the crystallization kinetics under steady shear flow conditions of different samples obtained by blending two isotactic poly(1-butene)s with different average molecular weights. It is observed that the addition of a small amount of high MW-polymer (< 10 wt%) to a low MW-sample does not produce any appreciable effect upon the crystallization kinetics under both quiescent and shear flow conditions. This behavior can be attributed to constraint release of high MW chains due to the relaxation of the shorter chains and can be described by the double reptation theory, which coupled with classical nucleation models allows for good quantitative predictions of the experimental results by using the relaxation times of the two blend components as the only fitting parameters.

Key words: polymer crystallization, flow-enhanced crystallization, nucleation, modelling

1 INTRODUCTION

Thermoplastic polymers are usually processed in the molten state under the action of complex flow fields. The application of these flow fields can strongly enhance the crystallization, the phenomenon is usually know as Flow-Induced Crystallization (FIC). It is generally accepted that the main action of the flow is in increasing the nucleation density, while the influence on the growth rate is less relevant.

In classical nucleation theory, the nucleation rate is a function of the free energy difference between liquid and crystalline phase; an increased nucleation can be explained in terms of ordering effect of the flow. It is obvious that properties affecting flow regimes will have consequences also on the crystallization kinetics. Among these factors, Molecular Weight (MW) is known to play a key role. According to the above picture, faster kinetics are found when MW is increased. The understanding of effect of Molecular Weight Distribution (MWD) is still at a primitive stage as it has been considered only in a limited number of works and they seem to indicated that the effect of constraint release, generated by the short chains with faster relaxation, must be accounted for

in order to understand the crystallization of polydisperse systems under flow conditions.

Theoretical predictive models for FIC usually rely on the assumption that the same expression for nucleation rate holds under both flow and static conditions provided that the free energy term is modified. In this view, micro-rheological models can be used to describe the flow-induced change in the free energy term and, therefore, the reduction in the characteristic time for nucleation under steady shear and extensional flows [1]. Polydispersity can accounted for by means of the double reptation approach [2] thus describing the faster relaxation due to constraint release. With these ingredients the model has, at least in principles, no adjustable parameters and can be used to describe several flow conditions, as based on sound physical arguments.

2 THE MODEL

The model for flow-induced crystallization used in this work is summarized in the following.

The model assumes that the effect of flow is mainly localized in the nucleation stages, as often verified experimentally [1]. A further assumption is that the effect of flow on the nucleation rate is merely

additive, thus reflecting in an increase of the thermodynamic driving force for nucleation. Under these assumptions, the free energy difference between liquid and crystalline phase appearing in the classical expression for the nucleation rate [3] is modified as follows:

$$\Delta G = \Delta G_q + \Delta G_f \tag{1}$$

where ΔG_q is the quiescent free energy change at the crystallization temperature and ΔG_f the flow-induced free energy change of the melt phase.

The explicit expression for ΔG_f is derived from the micro-rheological model of Doi and Edwards [4] using the so-called Independent Alignment Approximation (IAA) approximation. In this conditions the flow-induced excess free energy assumes a relatively simple form [5]:

$$\Delta G_f = 3ck_BT\int_0^\infty \dot{\mu}(s)A(\dot{\gamma}\cdot s)ds \tag{2}$$

In Eq.(2), kB is the Boltzmann constant, T the absolute temperature, $\dot{\gamma}$ the shear rate and c the entanglement density, which can be calculated as c = $(\rho N)/M_e$ where ρ is the melt density, N is the Avogadro number, and M_e the molecular weight between entanglements. A(x) is an integral function of the deformation history that, for steady-state shear conditions, is given by:

$$A(x) = \frac{1}{2}\int_0^1 \ln\left(\frac{1 + x^2\xi^2 + \sqrt{\xi^4(x^4 + 4x^2) - 2x^2\xi^2 + 1}}{2}\right)d\xi \tag{4}$$

μ is the memory function. The Doi-Edwards memory function for simple reptation is:

$$\mu(s) = \frac{8}{\pi^2}\sum_{p\ odd}\frac{1}{p^2}\exp\left[-\frac{p^2 s}{\tau_d}\right] \tag{5}$$

where τ_d is the characteristic "disengagement" time. In the present work, as we study blends of two components having very different Mw, the memory function has been determined by means of a "Double Reptation" mixing rule. In particular, we have used the following expression [2]:

$$\mu_d(s) = \left[\phi_H\cdot\mu_H(s) + (1 - \phi_H)\cdot\mu_L(s)\right]^2 \tag{6}$$

where ϕ_H is the volume fraction of the high Mw component in the blend.

The set of Equations form (1) to (6) can be used to calculate the free energy difference between liquid and crystalline phase under flow conditions and then, with the assumption that the induction time, t_i, is inversely proportional to the nucleation rate:

$$\dot{N} \propto \frac{1}{t_i} \tag{7}$$

In view of Eq.(7) and of the nucleation model of Lauritzen and Hoffman [3] written in the form suggested by Ziabicki [6], the model expression for the dimensionless induction time is given by:

$$\theta = \frac{t_{if}}{t_{iq}} \simeq \frac{\dot{N}_q}{\dot{N}_f} = \frac{1}{1 + \dfrac{\Delta G_f}{\Delta G_q}}\exp\left[\frac{K_n}{T(\Delta G_q)^n}\frac{1}{\left(1 + \dfrac{\Delta G_f}{\Delta G_q}\right)^n} - 1\right] \tag{8}$$

where K_n is a constant containing energetic and geometrical factors of the crystalline nucleus, n accounts for the temperature region where the homogeneous nucleation takes place, $\dot{N}_f$ and $\dot{N}_q$ are the nucleation rates under flow and quiescent conditions, respectively.

It is worth noting that the characteristic times τ_{dH} and τ_{dL} are the only parameters of the model; while in principle they can be obtained from the viscoelastic characterization, in practice they are determined by fitting the experimental induction times of the pure components with eq. (8). The model is then used to predict the dimensionless induction times of the blends.

3 MATERIALS AND METHODS

The materials used for the experiments are two commercial grades of isotactic poly(1-butene); the main difference between the two polymers lies in the molecular weights (which are in 7.4 : 1 ratio). For this polymer the molecular weight between entanglements, M_e, is 21,000 g/mol (as calculated from viscoelastic data). Some other relevant characteristics are reported in Table I.

In order to study the effect of molecular weight, and its distribution, several blends of BR200 (the high molecular mass sample, H) and PB800 (the low molecular mass, L) were prepared (in a twin-screw extruder with a rotational velocity of 40 rpm, a temperature profile ranging form 120 to 170°C, and an average residence time of 3 minutes.) The H content varies between 1.25 and 10 wt% and the blends are correspondingly labeled as *Blend x*

(where x is the weight percentage of polymer H.)

Table1. Some relevant characteristics of the iPB samples

	PB800 (L)	BR200 (H)
M_n [kg/mole]	37	125
M_w [kg/mole]	115	851
M_w/M_n	3.1	6.8
T_m [°C]	130.4	144.3
η_0@140° [Pa s]	757	288,500

Rheological experiments were performed using a strain-controlled rotational rheometer (ARES, TA Instruments) equipped with 25 and 7.9 mm parallel plates, using a gas-convection oven for the temperature control and a 2KFRT dual range torque transducer.

Isothermal crystallization experiments were conducted according to the following thermal protocol. After a thermal annealing at 160 °C for 10 min, the samples were cooled (at -10 °C/min) to the crystallization temperature, T_c = 95°C, for the isothermal experiments. At this temperature the solidification process was monitored measuring the sample viscosity.

Some Differential Scanning Calorimetry (DSC) experiments (not reported in the following section) were carried on out in order to evaluate the parameter K_n and the parameter n. For all the samples we used the values of $n = 1$, which is the typical value for crystallization under moderate undercooling and $K_n = 2.6 \times 10^{10}$ K J/m^3.

4 EXPERIMENTAL RESULTS AND MODEL COMPARISON

In figure 1 the complex viscosity master curves for the blends at the reference temperature of 140°C are reported; solid lines representing the pure unmixed high and low molecular mass polymers are also reported for comparison, showing that the mechanical degradation due to mixing is practically negligible. As expected, the linear viscoelastic behavior of the samples is typical of entangled linear polymer melts. The viscosity is an increasing function of the mass fraction of polymer H. It is noticeable that the viscosity curve of the sample *Blend 1.25* is completely superimposed on that of the sample *Blend 0* thus indicating that such a low fraction of high molecular mass component does not appreciably modifies the viscoelastic behavior of the system. The sample *Blend 5* has a viscosity higher than that of sample *Blend 0* and, in particular, its zero-shear viscosity is about 30% higher; thus

confirming that this sample is above the overlap concentration for long chain-long chain interaction. From the complex viscosity curves a characteristic relaxation time, defined as the reciprocal of the frequency below which Newtonian behavior is observed, can be extracted. This characteristic time, τ_η, is related to the disengagement time τ_d as they both reflect the time required for a molecule to escape from its topological constraint. The as-calculated relaxation times for samples *Blend 0* and *Blend 100* at the crystallization temperature of 95°C are approximately 3 and 1100 s, respectively.
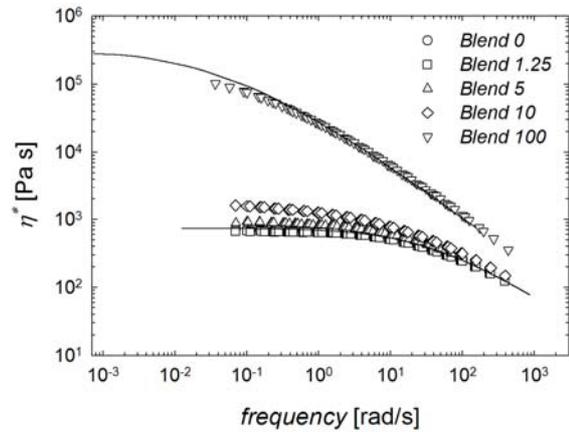

Fig. 1. Complex viscosity master curves at the reference temperature of 140°C. The lines refer to the pure (unmixed) H and L samples.

The crystallization kinetics under flow are measured using the so-called viscosity induction time. Once the crystallization temperature of 95°C is reached, a constant shear rate is applied and the polymer viscosity is measured. A viscosity induction time, t_i, is defined as the instant when the viscosity is twice its initial steady state value.

Typical flow-enhanced crystallization results are reported in figure 2, where the evolution of viscosity (normalized to its initial steady-state value, η_{ss}) is reported as a function of time for the sample *Blend 0* at different shear rates.

Figure 2 shows that above a critical shear rate the flow accelerates the crystallization kinetics and the induction time shifts to lower values.

Flow-enhanced crystallization results for the blends (concentration of H below 10%) are summarized in Figure 3 where the following features are evident:

i) under quiescent conditions (i.e., at vanishing shear rates) the high molecular weight polymer crystallizes three times faster than the low molecular weight polymer;

ii) for each sample there is a critical shear rate above which the flow accelerates the crystallization kinetics;

iii) this critical shear rate is lower for the high MW-sample than for the low MW-sample;

iv) the quiescent and flow-enhanced crystallization time of the blends does not significantly deviate from the value relative to the pure L polymer.
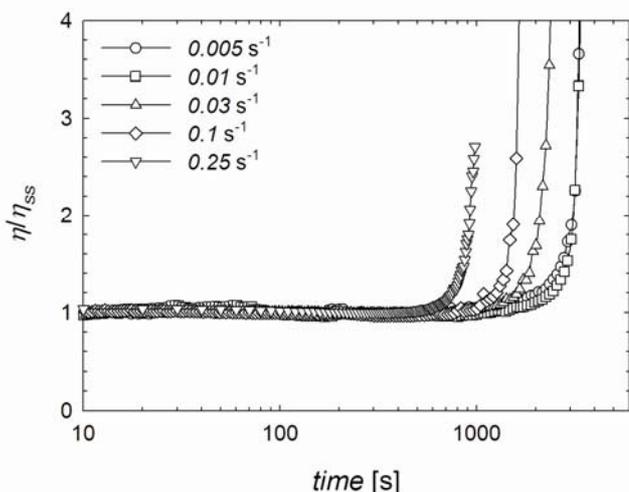

Fig. 2. Normalized viscosity as a function of time for the sample *Blend 0* at 95°C. Different symbols refer to different shear rates as reported in the legend.
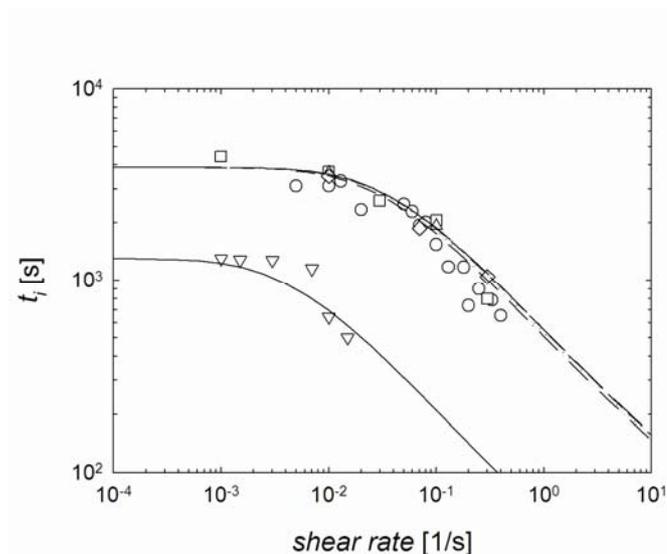

Fig. 3. Induction time as a function of the shear rate at 95°C. Symbols as in figure1. Lines through data points are model calculations.

Model calculations are performed using the

disengagement times of the pure components of the blends, τ_{dH} and τ_{dL}, as the only fitting parameters; afterwards, the double reptation memory function is used to predict the behavior of the blends. With this procedure the curves reported in figure 3 are obtained. The agreement between the model calculations and the experimental results is good; in particular, the model is able to capture the transition from the low shear rate plateau to higher shear rate flow-enhanced crystallization zone and to predict the scarce effect of low concentration of polymer H. The latter feature is related to the effect of constraint release that is correctly described by the double reptation memory function they appear in the text.

A remark concerns the quantitative values of the relaxation times that were derived from the best fit procedure. In fact, the best estimate procedure yield values of the H and L disengagement times of $\tau_{dH} = 1700$ s and $\tau_{dL} = 200$ s, respectively. These values only partly agree with those obtained from the viscoelastic characterization of the blend components. This lack of coherence can be attributed to different factors and it is still under investigation.

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