Analysis of flow induced crystallization through molecular stretch

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ABSTRACT

In this work, specific experiments on an isotactic polypropylene are carried out, aiming to investigate the flow induced crystallization and the final morphology. The viscoelastic nature of the polymer is described by a non-linear Maxwell model applied to the conformation tensor. Shear stress evolutions, recorded during step shear isothermal experiments, are satisfactory described considering the molecular stretch, i.e. the difference between the two main eigenvalues of the conformation tensor. In the general model, the effect of temperature, pressure, and crystallinity are taken into account. Furthermore, a modeling framework is proposed to describe flow-induced crystallization of isotactic polypropylene. The spherulitic growth rate is analyzed on the basis of a flow dependent equilibrium melting temperature, using the molecular stretch as the key parameter. A phenomenological correlation of the nucleation rate with growth rate is observed. By combining the morphological models, both for nucleation and growth rate, for flow induced crystallization is possible to explain the effect of shear rate and shearing times in different experimental results, and potentially in the simulation of polymer processing.

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1. Introduction

Many characteristics of polymeric products are determined by morphology distribution induced by their manufacturing process [1,2].

The evolution of morphology is determined by the thermo-mechanical history up to solidification [3,4], which in polymer processing operations may take place at very high cooling rates and pressures and under the effect of flow. This framework is even more complex for thermoplastic materials like isotactic polypropylene, i-PP, in which different crystalline phases and different morphologies can coexist. Dominantly present in i-PP is typically the α-phase [5,6], between three different ordered crystalline phases, formed at atmospheric pressure and low to moderate cooling rate.

Indeed, in the last decades, large interest was devoted by researchers to clarify main aspects of the effect of cooling rate, pressure and flow on morphology evolution of thermoplastic polymers [7—12].

Experimental observations were carried out by different research groups over the years, by using essentially two protocols: continuous flow, in which the material undergoes to deformation

for most of the crystallinity evolution time [13,14]; step shear flow, in which the deformation is imposed for a short time [15—18]. The latter protocol may separate the effects of flow on the molecular stretch from the effects of crystallization on the rheological behavior [19—21].

According to the current understanding, the effect of flow on crystallization may be schematized as follows:

 i) There is a threshold below which morphology evolution keeps quiescent features;
 ii) Above such a threshold, nucleation density and growth rate are affected by the flow;
iii) Above a second threshold, crystallization features change into fibrillar morphology and related fibrillar crystallization kinetics.

Furthermore, it is widely recognized that the effect of flow on crystallization kinetics has to be related to molecular stretch, whose evolution determines nucleation density and spherulitic growth rate and, thus, the evolution of morphology up to solidification. Indeed, the values of the thresholds identified above are normally related to the Weissenberg number [22] which, comparing the characteristic times of flow intensity and molecular relaxation, gives an idea of the capacity of flow to orient and stretch the macromolecules.

A literature survey of the current models for flow-induced

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crystallization (reviews are given by Pantani et al. [7] and by Peters et al. [22]) shows that in order to describe the enhancement of crystallization kinetics induced by flow it is necessary to model the effect of flow on molecular conformation (by means of a viscoelastic model) and the nucleation and growth of crystalline structures.

In this work, a model for the evolution of morphology during crystallization is proposed on the basis of the simple model of molecular stretch evolution reported in Ref. [7]. Furthermore, experiments of i-PP Flow Induced Crystallization are carried out in this work with the aim of characterizing the parameters of the model and comparing the model predictions with final solidification morphology.

2. Experimental

2.1. Material

The material adopted in this work was an i-PP (tradename of Moplen T30G, supplied by Montell). This resin is a general-purpose homopolymer for extrusion/molding applications, with a melt flow index equal to 3.6 (ASTM D1238/L). The molecular weight distribution was determined by a size exclusion chromatography as weight-average molar mass M_w of 376 kg mol^{-1}, polydispersity index M_w/M_n of 6.7, and meso pentads content 87.6%. The glass transition temperature (T_g) and melting temperature of Moplen T30G reported on the material datasheet are -15 °C and 166 °C, respectively. The rheology and the crystallization kinetics of the same resin were the focus of several studies [23–29].

The steady state viscosity of the polymer melt was well described by a Cross model [7].

$$\eta(T,P,\chi,\dot{\gamma}) = \frac{\eta_0 \alpha_v(T,P,\chi)}{1 + C[\eta_0 \alpha_v(T,P,\chi)\dot{\gamma}]^{1-r}} \tag{1}$$

where $\dot{\gamma}$ is the shear rate and the shift factor, $\alpha_v(T,P,\chi)$, which takes into account the changes due to temperature, T, pressure, P, and relative crystallinity degree [21], χ, was given by a modified WLF equation,

$$\alpha_v(T,P,\chi) = \exp\left[-\frac{D_1(T-T_0)-D_3P}{D_2+(T-T_0)} + D_4\chi^{D_5}\right] \tag{2}$$

The parameters to be used in Eqs. (1) and (2) are listed in Table 1.

The material was characterized in the literature for quiescent crystallization (nucleation density, growth rate, and mesomorphic crystallization rate) also under very high cooling rates and pressure [7–9,30]. Under quiescent conditions, the nucleation was found to have a heterogeneous character; indeed, the nucleation density was verified to be a function of temperature only [8,31].

2.2. Methods

The effect of flow on the spherulitic crystallization of the material was assessed in the literature [7]. In particular, in a recent paper [32], step shear tests were conducted in the Linkam shearing

Table 1
Parameters adopted to describe viscosity of i-PP resin T30G.

Parameter	Value	Parameter	Value
D_1	4.006	η_0 [Pa s]	6387
D_2 [K]	301.4	C	0.0023
D_3 [K bar^{-1}]	0.6811	r	0.34
D_4	180	T_0 [K]	503
D_5	2		

device (parallel plates configuration) imposing a given plate rotation speed for a given time at the temperature of 140 °C. Due to the geometrical configuration of the system, since in plate-plate configuration the gap between the top and the bottom plates is constant, the shear rate varies linearly with radius, so there is a radial distribution of the shear rate. Shear rates in the range 0–8 s^{-1} were imposed to each sample, for shearing times chosen in the range 10–40 s [32]. The distribution of diameters of spherulites inside the samples was then characterized by means of optical microscopy. Those results [32] will be used in this work to validate the model for flow-induced crystallization.

Some data of morphology distribution in samples subjected to shear flow were also collected in this work. In particular, a Multipass Rheometer (MPR) [10] was adopted as a device able to impose a given shearing history to the samples. This MPR was developed at the Technical University of Eindhoven and was equipped with a slit geometry 120 mm long, 6 mm wide and 1.5 mm thick. The thermal history experienced by the material is reported in Fig. 1. The material was held above its equilibrium melting temperature at 220 °C for 10 min, in order to erase the effects of previous thermo-mechanical history. Subsequently, it was cooled down, with a cooling rate of 10 °C min^{-1}, to the test temperature, $T_s = 140$ °C, at which it was kept for 1 h. The material was then cooled to room temperature, which was reached about 5 min after the cooling start. Also in this case, the flow was applied soon after reaching 140 °C and according to a step-shear protocol, also represented in Fig. 1: after about 2 s from the start of the isothermal step, a constant velocity was imposed to the pistons and thus the material inside the slit was forced to reach a constant average velocity, $v_{av} = 1$ mm s^{-1}. This velocity was held for shearing times, t_{shear}, of 1 s and 20 s.

The samples solidified inside the MPR were cut by a microtome in order to obtain thin (20 µm) slices in-plane flow (parallel to the slice plane) at known distances from the skin. These slices were then characterized via polarized optical light microscopy.

Since the model for flow-induced crystallization presented in this work relies on the assessment of molecular stretch, it was necessary to validate the viscoelastic parameters of the material. To this goal, some data of shear stress in unsteady conditions were collected in this work. The device used is an ARES (Rheometrics) rheometer with a cone-plate configuration at the constant temperature of 140 °C. The tests were carried out according to the protocol reported in Fig. 2: a shear rate of 0.01 s^{-1} was kept
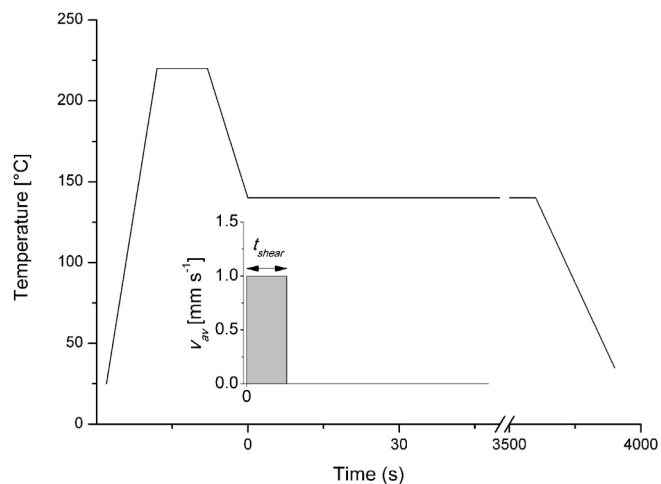

Fig. 1. Schematics diagram for temperature and shear protocols adopted with Multi Pass Rheometer (MPR).