Flow-induced crystallization of isotactic polypropylene: Modeling formation of multiple crystal phases and morphologies

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ABSTRACT

A modeling framework is presented to describe flow-induced crystallization of isotactic polypropylene at elevated pressures in multiple crystal phases and morphologies. By combining two models for flow induced crystallization developed in previous work, all parameters but one are a priori fixed. In the present work only one additional parameter was introduced, determining the portion of spherulites nucleated by flow that form β-crystals.

Model calculations show good agreement with experimental data for crystal volume fractions of all phases over a very wide range of flow-conditions, with shear rates varying from 0 to 200 s^{-1}, pressures varying from 100 to 1200 bar and shear temperatures from 130 to 180 °C. Moreover, the model provides a tool to investigate two open questions regarding crystallization of isotactic polypropylene. First, it is shown that flow-induced formation of β-phase can be accurately described by assigning a fixed portion of flow-induced spherulites to the β-phase. Due to the high growth rate of β-phase compared to the α and γ-phases, although over a relatively narrow temperature range, only a seemingly small portion of 0.2% of all flow-induced nuclei becoming β-spherulites is enough to explain the experimentally observed volume fractions of β up to 20%. Secondly, it is shown that experimentally found volume fractions of γ-phase at high shear rates and pressures can only be matched if γ-crystals can directly nucleate on highly oriented flow-induced crystallites (so-called shish).

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1. Introduction

In polymeric products, in particular those made from isotactic polypropylene, different crystalline phases and different morphologies can be present. In stereoregular isotactic polypropylene, four different crystal phases can be present. Most dominantly present is typically the α-phase [1], formed at atmospheric pressure and low to moderate cooling rate. Crystallization under the influence of moderately strong flow conditions or specific nucleating agents can induce β-phase [2], while crystallization of the γ-phase can be achieved in several manners such as small amounts of 1-olefine counits [3], introducing stereo- and regio-irregularities controlled by a metallocene catalyst [4,5], in materials of very low

molecular weight [6], or crystallizing under elevated pressure and high temperature [7,8]. Especially the latter is relevant in the context of the present work. Additionally, the formation of stable crystal phases can be suppressed in favor of a mesomorphic phase [9,10] at high cooling rates (>100 K/s). For completeness, we should also mention the recently discovered $\delta-$ phase (in isotactic polypropylene with long branches [11]) and $\varepsilon-$ phase (in stereo-defective polypropylene [12]).

Obviously, the occurrence of the mentioned crystal phases in a particular polymer product strongly depends on processing conditions. Factors like flow below the melting temperature [13–22], pressure [8,23,24] and of course temperature history [25–30] all play an important role. The classical example is injection molding. An extended set of the effects of processing conditions during injection molding and of molecular variations and their influence on phase composition of the final product was presented in a paper by Housmans et al. [31].

Modeling flow induced crystallization of polymers is inevitable for the prediction of final structure properties as a function of the local thermal and mechanical history which, in turn, determine to a

large extent the final local mechanical and optical properties of a polymeric product [31–33]. Such models do exist in literature, although they are usually focused on either the temperature effect [26,34], or the flow-effect (via an increase of nucleation density or enhanced crystallization rate) [35–48]. However, there are two important requirements for a reliable application of these models 1) experimental validation at process conditions, i.e. high pressure, high cooling rates and strong flow gradients and 2) the ability to predict a local mixture of different crystalline phases ($\alpha,\beta,\gamma,$ and meso-phase in isotactic polypropylene) as well as different crystalline morphologies (spherulites, shish-kebabs with lamellar branching, i.e parent and daughter lamella). Models based on molecular dynamics simulations do not fulfill the first requirement (see for example ref. [49], where the shear rates considered are <1 s^{-1}, not comparable to 10^2–10^4 s^{-1} as can be found in real processing conditions). With respect to the second one: to our knowledge such models do not exist!

The present model, which deals with the two issues of validation and multiple phase/multiple morphologies, combines two phenomenological approaches to flow induced crystallization of isotactic polypropylene that have been validated in previous works; non-isothermal crystallization leading to varying compositions of crystal phases (α, β, γ, meso) [24] and flow-induced structure formation leading to various crystalline morphologies (spherulite, shish-kebab with parent and daughter crystals) [50,51]. Aside from the obvious goal of validating the approach of combining these models, this research is also aimed at investigating two phenomenon specific to flow-induced crystallization of isotactic polypropylene.

1. Flow-induced beta-phase formation. In quiescent conditions only appearing if a specific nucleating agent is present, small fractions of beta-phase can also be formed in relatively mild flow conditions [52]. In the present model, this is captured by assigning a fixed portion of flow-induced nuclei to the β-phase. In this research we wish to investigate how big the fraction of flow-induced nuclei is that form beta-crystallites.
2. Nucleation of γ-phase on shish. It has recently been observed that under strong flow conditions at high pressure, relevant to e.g. the injection molding process, γ-crystals can have strong preferential orientation of 40° with respect to flow direction [53]. However, it is not clear whether gamma crystals only nucleate on kebabs formed by α-crystals, or if they can also nucleate directly on the shish. The formulation of the present model allows us to see effects of both possibilities on the phase composition.

2. Experimental

The model presented in this paper is validated with a set of experimental data that was previously published and described in detail in Refs. [52,54]. The experiments were performed in the Pirouette apparatus [52,54,55]. This extended dilatometer can be used to monitor specific volume of a material at a range of temperatures and pressures, and it possesses the added ability to subject the material to shear flow in a Couette cell.

The experimental protocol is as follows: starting from the molten state, $T_m = 230\,°C$, the material is cooled down at ~1 °C/s to room temperature under isobaric conditions at four different pressures ($p = 100,500,900,1200$bar). During cooling, a shear pulse was applied with fixed duration of 1 s and varying shear rate of $\gamma=0,3,10,30,100,180$ s^{-1} at undercooling of 30 °C or 60 °C. The undercooling is the difference between the temperature where the shear pulse was applied and the melting temperature, taking into

account for the variation of melting temperature with pressure according the Clapeyron equation [56] (Eq. (3)). The melting temperature at atmospheric pressure was taken as 197 °C. All experimental conditions are summarized in Table 1. The specific volume of the material was monitored and the experimental crystallization temperature was defined as shown in Fig. 1 [54]. determined that this point corresponds to a space filling of ~10%.

The effect of the flow on the crystallization kinetics is expressed by the dimensionless transition temperature Θ,

$$\Theta = \frac{T_c^{\dot\gamma}}{T_c^Q}, \tag{1}$$

with T_c^Q the crystallization temperature in quiescent conditions and $T_c^{\dot\gamma}$ the crystallization temperature after shear. Hence, $\Theta = 1$ if shear has no effect and Θ increases with shear rate.

Ex-situ wide Angle X-ray Diffraction (WAXD) and small angle X-ray scattering (SAXS) single-shot experiments were performed on the solidified samples at the Dutch-Belgian (DUBBLE) beamline BM26 [57] of the European Synchroton Radiation Facility (Grenoble, France) using a high resolution Pilatus 1M detector and a wavelength of $\lambda = 1.033$ Å. Two-dimensional images were acquired and corrected for spatial distortion and for the scattering of the empty sample cell [52]. Volume fractions of α,β, and γ-phase were obtained from WAXD images as described by van Erp et al. [52]. The SAXS results are not used in this paper.

2.1. Material

The material used in the study is an iPP homopolymer (Borealis HD601CF, $M_w = 365$ kg mol^{-1}, $M_n = 68$ kg mol^{-1}), the material of choice of many other crystallization studies as well [51,52,58]. The model used in this work calculates nucleation rate and longitudinal shish growth rate from backbone stretch on a continuum level. The former is calculated from stretch of a mode representative of the longest chains in the material, the latter from stretch of an average mode. The eXtended Pom–Pom (XPP) model [59] is used to calculate the backbone stretch, with parameters for the XPP model as given by Roozemond et al. [51].

3. Crystallization model

The concept of the model presented in this paper was presented by van Drongelen et al. [24]. For each crystal phase, the Schneider rate equations [26,60] are solved to calculate the crystallization kinetics. To do so, only temperature dependent nucleation density and growth rate are required. The growth rate of the α, β, and γ-polymorphs was determined by van Drongelen [24]. The kinetics of formation of the mesomorphic phase were also determined, but will not be used in this paper since the experiments used do not

Table 1
Overview of all experimental conditions.

Pressure (bar)	Undercooling	Shear temperature	Shear rates
	$\Delta T_{\dot\gamma}$ (°C)	$\Delta T_{\dot\gamma}$ (°C)	$\dot\gamma$ (s^{-1})
100	30	167	0, 10, 30, 100, 180
500	30	179	0, 10, 30, 100, 180
900	30	190	0, 10, 30, 100, 180
1200	30	201	0, 10, 30, 100, 180
100	60	137	0, 3, 10, 30, 100, 180
500	60	149	0, 3, 10, 30, 100, 180
900	60	161	0, 3, 10, 30, 100, 180
1200	60	170	0, 3, 10, 30, 100, 180