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Shear-induced nonisothermal crystallization of low-density polyethylene

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Abstract

The effect of melt memory on the shear-induced nonisothermal crystallization of a low-density polyethylene melt is analyzed with a shear DTA instrument. The melt state responsible for the saturation of shear-induced isothermal crystallization was identified previously as the steady state in steady shear flows and the strain applied to the melt was identified as the controlling factor for that saturation. Here it is shown that the same strain that saturates the isothermal crystallization also saturates the shear-induced nonisothermal crystallization. Regardless of the cooling rate, the nonisothermal crystallization, starting from the same sheared melt temperature, saturates at the same strain. The contribution of the melt memory effect to the overall nucleation density is estimated, and it is concluded that the majority of nuclei results from the thermal-induced crystallization.

Keywords: Shear flow; Nonisothermal crystallization; Shear DTA

1. Introduction

The current view of polymer crystallization in real processing conditions is that it is nonisothermal with strong thermal gradients, the material microstructure being formed during the cooling process. From a practical point of view, the study of shear-induced nonisothermal crystallization and the conditions leading to the saturation of crystallization kinetics are important for controlling the final product properties. To our knowledge, the effect of melt memory on shear-induced nonisothermal crystallization was not considered so far. In fact, little attention has been given to the melt morphology prior to cooling. It is our opinion that this morphology plays a key role during the overall crystallization development, both isothermal and nonisothermal, since it must be related to the formation and dimensions of precursor structures.

Probably because of the difficulties in mimicking precisely the combined effects of orientation induced by the flow and the relatively high cooling rates in real processing, only a few works on shear-induced nonisothermal crystallization have been reported. Some relevant results will be briefly presented. A parallel plate rheometer, incorporating a differential thermal analysis setup, was used to record the shear-induced nonisothermal crystallization of isotactic polypropylene (iPP) at low shear rates [1]. Besides the expected conclusion that shear flow accelerates the crystallization kinetics, no other relevant result was reported in this work. The same conclusion was drawn for the effect of pre-shear treatment on the shear-induced nonisothermal crystallization of both neat iPP and a microfibrillar blend with iPP and PET studied by on-line small angle X-ray scattering [2]. Also for the nonisothermal crystallization of iPP, besides the already mentioned acceleration of crystallization with the pre-shear treatment, other results obtained with a custom dilatometer indicate less oriented samples and the crystallization temperature onset increases with the temperature of application of shear [3]. It was concluded that application of shear at a sufficiently high temperature (always during the cooling process and at a temperature below

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the melting temperature) resulted in the remelting of "flow-induced crystalline structure" and relaxation of oriented chains.

The last conclusion implicitly assumes that flow-induced precursor structures have crystalline order. To our knowledge, there is no experimental evidence for this assessment. Nevertheless, it must be mentioned that micro-WAXS experiments performed at different positions on iPS samples, nearby the regions of a pulled fibre, after shearing at 260 °C, followed by a quenching at room temperature after the cessation of the flow, indicate the presence of a crystallinity level of less than 1% [4]. Since these micro-WAXS experiments were performed on quenched samples, and not at the molten state, they do not provide a clear indication of the precursor structures' crystallinity, even though at the slow crystallizing rate of this polymer.

However, there is no doubt that ordered structures exist in sheared melts. It was shown that the flow-induced oriented structures above nominal melting temperature must be non-crystalline or of low crystallinity, below the crystallinity detection limit in WAXS, and that ordered structures, with crystalline order, develop after application of shear at temperatures below the polymer nominal melting temperature [5]. There is also experimental evidence that precursor structures without crystalline order persist for long time after cessation of shear, even when shear is applied at temperatures above the polymer melting temperature [5,6].

To get further insight into the melt morphology, possible mechanisms behind the formation of shear-induced precursors and their effect on crystallization development, it is important to separate undercooling effects, *i.e.* the application of orientation imposed at temperatures below the melting temperature, from the melt orientation at the common processing temperature. This implies the study of melt memory effects induced by shear flow on crystallization.

The term melt memory has been used to describe the effect of different holding times at the melt temperature on quiescent crystallization kinetics. It is known that increasing this time or the melt temperature, the crystallization kinetics decreases. After a time long enough at a specified melt temperature, no change is observed on crystallization kinetics [7]. It is said that the melt memory was erased. The reason for this behaviour was assigned to clusters existing in the melt, and theories for the cluster distribution were presented [8]. An important point is the molecular origin of these clusters, which was never clearly established so far. Since they were generated by flow deformation of the melt, there is no reason to assign their specificity to crystallization from quiescent melts. Their molecular origin could be studied by analyzing the effect of controlled shear deformations on melts with erased memory. One would expect to observe the reverse effect – an acceleration of crystallization kinetics.

Previous studies on shear-induced isothermal crystallization of a low-density polyethylene and iPP described this acceleration [9,10]. Contrary to current experimental procedures, controlled shear deformation was applied at a temperature higher than the thermodynamic melting temperature, after which the sheared melt was cooled to the crystallization temperature and crystallization kinetics was recorded with a shear DTA instrument [11]. It was shown that a critical strain was required to saturate the crystallization kinetics, its magnitude being crystallization temperature independent, but decreasing with the sheared melt temperature increase. For higher melt temperatures, crystallization saturates at lower strains. The melt state responsible for this saturation was identified by shear stress growth experiments as the steady state in steady shear flow, where for linear polymer chains the viscosity is constant with time. The strain at the onset of this state is similar in magnitude and shows the same temperature variation as that needed to saturate crystallization. By saturation it is meant that crystallization process cannot be further accelerated.

Acceleration of crystallization implies an increase in the density of nuclei. The density of nuclei is limited for two reasons, because for any crystallizable material stable nuclei must reach a critical size and the quantity of material available for phase change is finite. A significant part in the density of nuclei results from the supercooling degree, and it may be evaluated with quiescent crystallization experiments. The remaining contribution results both from the effect of melt memory and from the shear deformation applied to the supercooled melt. The separate role of these two contributions to the overall nucleation density was not established so far.

Janeschitz-Kriegl considered the mechanical work or the shear stress as the main factor responsible for the density of nucleation increase, up to a limiting value [12]. Kornfield et al. reported the saturation of crystallization kinetics when shearing was applied above a critical stress for a time longer than a critical duration [13]. For higher stresses or longer shearing time a transition to oriented growth was observed. Bushman and McHugh performed planar extension experiments and identified a limiting critical strain for oriented crystallization [14]. It was found that accelerated kinetics, development of oriented growth, and the existence of a limiting strain for oriented crystallization are observed both in shear and in extensional flows [13]. A question remains concerning the factor responsible for the acceleration of shear-induced crystallization kinetics: the shear stress, the stress dependent shearing time or the shear strain. Chai et al. performed small angle light scattering experiments with a polyethylene in a Linkam shearing cell and observed the saturation of the spherulite radius $R(\dot{\gamma})$, with a value around 1/2 the radius of the spherulite without shear, at strains of $\sim 10^3$ s.u. [15]. Similar strains also lead to the anisotropy saturation of SAXS patterns of PE and PP melts with DBS, when sheared in a Linkam shearing cell [16]. In previous works we clearly identified the strain applied to the sheared melt as the factor responsible for the acceleration of crystallization kinetics and its saturation [9,10].

In this work we study the effect of melt memory on shear-induced nonisothermal crystallization of a low-density polyethylene melt. The relevance of two important effects on the overall crystallization kinetics development, the memory of orientation imposed on sheared melts and the cooling rate is