

Polymer Communication

Shear-induced nonisothermal crystallization of low-density polyethylene

Weidong Zhang^{a,b}, José A. Martins^{a,b,*}^a *Departamento de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal*^b *CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal*

Received 29 June 2007; received in revised form 25 July 2007; accepted 13 August 2007

Available online 19 August 2007

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.

© 2007 Elsevier Ltd. All rights reserved.

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

* Corresponding author. Departamento de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal. Tel.: +351 253510325; fax: +351 253510339.

E-mail address: jamartins@dep.uminho.pt (J.A. Martins).

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

analyzed. The following questions will be answered. (i) What is the effect of the sheared melt temperature on the nonisothermal crystallization kinetics? (ii) Does this crystallization saturates, and if so, what is the effect of the cooling rate? (iii) What is the correspondence between the critical strains eventually needed to saturate the shear-induced nonisothermal crystallization and those that saturate the shear-induced isothermal crystallization for the same temperature of the sheared melt?

2. Experimental

The material used is a low-density polyethylene (ref. PE7324 from Boralis, MFI = 3.3 g/10 min, with a load of 2.16 kg, ISO 1133) with a thermodynamic melting temperature of 133.6 °C. Further material details and results of melt memory effect on shear-induced isothermal crystallization were given in Ref. [9].

The shear-induced crystallization experiments were performed with a shear DTA instrument whose working principle was already described in detail [11]. In this instrument, the molten polymer was initially pumped from an accumulator to the capillary channel at shear rates lower than 0.5 s^{-1} , until the channel was full with molten material. After a fixed relaxation time of 5 min, shear pulses with different durations and intensities were applied above nominal melting temperature, after which the material was immediately cooled with constant and controlled cooling rates (from -2 °C/min up to -8 °C/min), and the overall crystallization kinetics was recorded. Both flow and temperature profiles on the flowing polymer melt are perfectly stabilized in the measurement region of the shear DTA capillary channel. The apparent shear rate at the wall was corrected with the Rabinowitsch correction for the non-Newtonian behaviour of the material. The true shear rates were used to evaluate the strains applied to the melt with an accuracy of $\pm 10\%$.

Rheometer experiments were performed in a Physica MCR 300 rheometer (Paar Physica) with parallel plate configuration (25 mm diameter). Following a temperature calibration procedure described previously [17], the temperature accuracy is $\pm 1 \text{ °C}$.

3. Results

3.1. Shear DTA results

Fig. 1a shows the nonisothermal crystallization of polyethylene at the cooling rate of -4 °C/min , after a pre-shear at 220 °C with different shear rates and constant shearing time 60 s. Results obtained when a constant shear rate ($\dot{\gamma}_{w,a} = 8.4 \text{ s}^{-1}$) is applied during different shearing times are shown in Fig. 1b. The crystallization kinetics is accelerated (shifted to higher temperatures) with the increase of shear rate or shearing time. As observed previously for shear-induced isothermal experiments [9,10], the saturation occurs at a limiting critical strain. The strain value evaluated is around 3090 s.u. Surprisingly, for shear-induced isothermal crystallization, a similar value of the critical strain was recorded for the

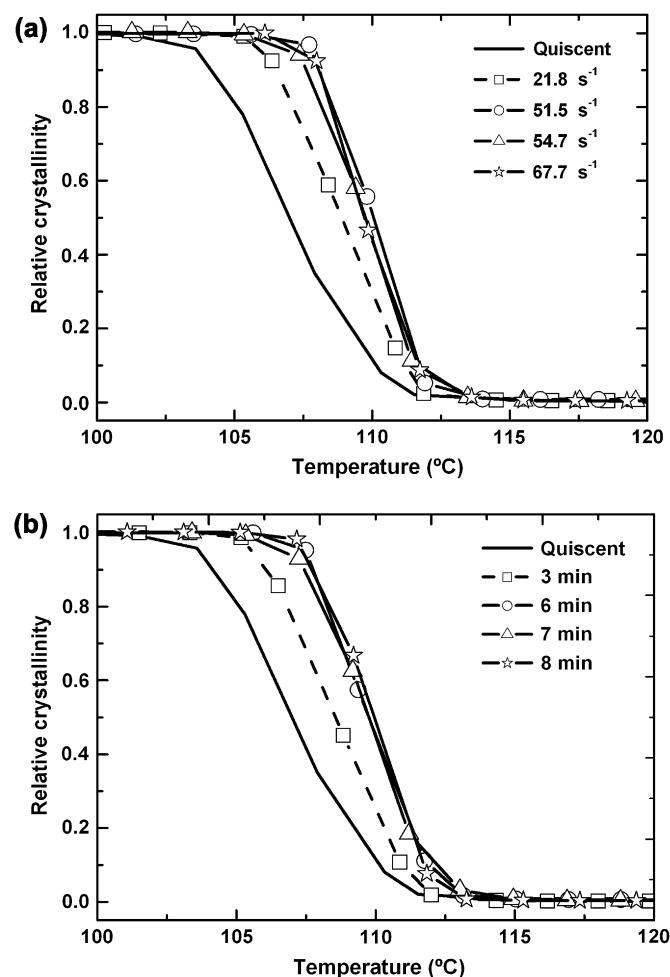


Fig. 1. Nonisothermal crystallization at constant cooling rate of -4 °C/min after controlled shearing at 220 °C . (a) Constant shearing time (60 s) and increasing shear rates. The kinetics saturates at a shear rate at the wall $\dot{\gamma}_w = 51.5 \text{ s}^{-1}$, corresponding to an average critical strain at the wall of 3090 s.u. ($\pm 10\%$). (b) Constant shear rate at the wall (8.3 s^{-1}) and increasing shearing times. The average critical strain at the wall is 2988 s.u. ($\pm 10\%$).

saturation of crystallization from a sheared melt at 220 °C (Table 1). In fact, within the measurements of experimental errors, it may be considered that isothermal and nonisothermal shear-induced crystallizations saturate at the same strain. The strain applied to the sheared melt is the factor controlling the saturation of crystallization.

The effects of sheared melt temperature and cooling rate are analyzed in Fig. 2a and b, respectively. The results

Table 1

Average critical strains measured with the shear DTA (at the wall, $\bar{\gamma}_w$) and with a rheometer, in parallel plate configuration (at $r=R$, $\bar{\gamma}_{r=R}$), for the saturation of isothermal, nonisothermal crystallization and stress growth experiments, respectively

$T \text{ (°C)}$	Shear DTA		Rheometer
	Nonisothermal $\bar{\gamma}_w$	Isothermal $\bar{\gamma}_w$	Parallel plate $\bar{\gamma}_{r=R}$
190	—	—	6376
200	5838	5888	5848
210	4152	4061	4054
220	3090	2916	3032

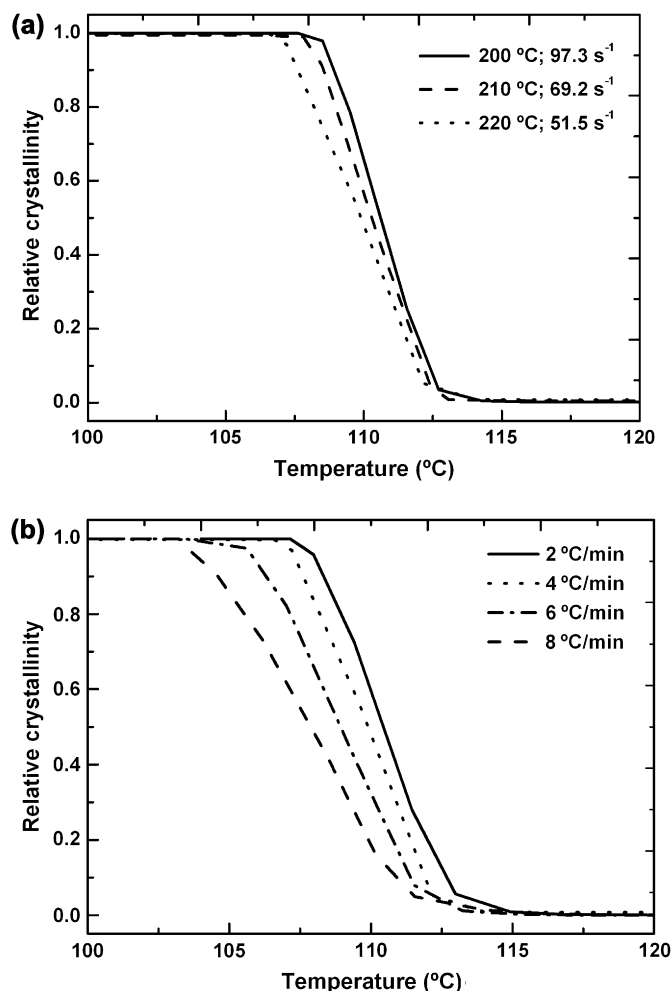


Fig. 2. Effect of shearing temperature and cooling rate on saturation of non-isothermal crystallization kinetics. (a) Saturation of crystallization at constant cooling rate of 4 °C/min for different shearing melt temperatures. The shearing time is 60 s and the average critical strains are 5838 s.u., 4152 s.u. and 3090 s.u. for 200 °C, 210 °C and 220 °C, respectively. (b) Saturation of non-isothermal crystallization at different cooling rates and the melt temperature of 220 °C for constant shearing time of 60 s and the shear rate of 51.5 s⁻¹. The average critical strain is 3090 s.u. The measurement error in the strain values is $\pm 10\%$.

indicated for each cooling rate and melt temperature refer to the saturation of crystallization conditions. Those of Fig. 2a were obtained for constant cooling rate of -4 °C/min and shearing time of 60 s. They indicate that the strain needed to saturate crystallization decreases with the sheared melt temperature increase (Table 1). On the contrary, for a constant sheared melt temperature, the saturation of crystallization is not affected by the cooling rate (Fig. 2b). Regardless of the applied cooling rate, kinetics saturates at the same applied strain ≈ 3090 s.u., corresponding to an applied shear rate at the wall of 51.5 s⁻¹ and a shearing time of 60 s.

3.2. Sheared melt at steady state

The coincidence of strain values leading to the saturation of both isothermal and nonisothermal shear-induced

crystallizations further confirms that a well defined melt state should be responsible for this behaviour. This melt state was identified by rheometer experiments as the steady state in steady shear flows [9,10]. The strains at the onset of this state are shown in Fig. 3. For a specific melt temperature they are similar to those needed to saturate crystallization (see Table 1). The experimental procedure to obtain these results was described in detail [9,10]. At steady state the viscosity is constant with time.

Although the strain in the capillary and that in the rheometer plate changes with the capillary or plate position, being maximum at the capillary wall or plate radius, respectively, it must be noticed that the strain that saturates crystallization is exactly that needed to establish a steady state in shear flow. It may easily be checked in a shear stress growth experiment that the strain at the onset of steady state is independent of the plate diameter used. It is a material property, dependent on polymer molecular weight and branching degree, chemical structure and interchain interactions. Therefore, one would reasonably expect that the strain needed to saturate crystallization would also be independent of the capillary diameter used.

4. Discussion

A recent work reported molecular dynamics simulation results of crystallization and orientation in PE during uniaxial extension [18]. Although in shear flows the maximum extension allowed to polymer chains is around $0.5L$, where L is the chain length, while in extension flows this extension may be $0.95L$ [19], the above results allow us to understand the effect of deformations on the melt morphology and hence their effect on crystallization kinetics. It was found that crystallization process accelerates as a result of large deforming stresses that drive the chains to lower conformational energy states, by aligning long *trans* sequences in a single direction. It was further concluded that extension and orientation of large segments of the chains reduce the barrier to primary nucleation and that a sufficient total strain is required to extend the

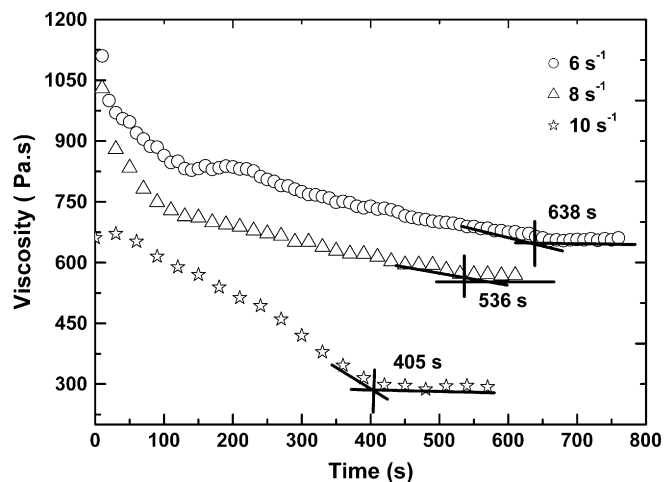


Fig. 3. Shear stress growth experiments at 210 °C with the shear rates indicated.

polyethylene chains and align the chain segments parallel to each other. Above a threshold strain, sufficient extension and orientation develop that allow rapid nucleation as soon as deformation is stopped [18].

As mentioned in Section 1, the reason behind the acceleration of crystallization from sheared polymer melts is commonly assigned to the increase of nucleation density. The overall nucleation density increase results from three factors: the orientation imposed to the sheared melt at the processing temperature, the additional deformation imposed to the supercooled melt, and the increase resulting from the supercooling, which is determined solely by the crystallization conditions, isothermal or nonisothermal. The maximum contribution of the last factor to the overall nucleation density is around 10^{10} nuclei/m³ [12]. The deformation imposed at the processing temperature contributes to a maximum of around 10^2 nuclei/m³. Since the maximum nucleation density is around 10^{18} nuclei/m³ [12], it remains that around 10^6 nuclei/m³ are originated by shear deformation imposed at the supercooled melt, generally at temperatures below the melting temperature and nearby the average crystallization temperature.

Although it is important to understand the effect of melt memory on shear-induced crystallization, as well as the melt morphology at steady state and the dimensions of precursor structures at this state, its contribution to the overall nucleation density is low, no more than the 10^2 nuclei/m³ mentioned above. This conclusion may already be extracted from the results in Fig. 1a and b: the temperature increase due to the deformation applied at the molten state is small, ≈ 3 °C.

Results in Fig. 4 show the variation of the half crystallization temperature with cooling rate for quiescent nonisothermal crystallization experiments performed with a Perkin–Elmer

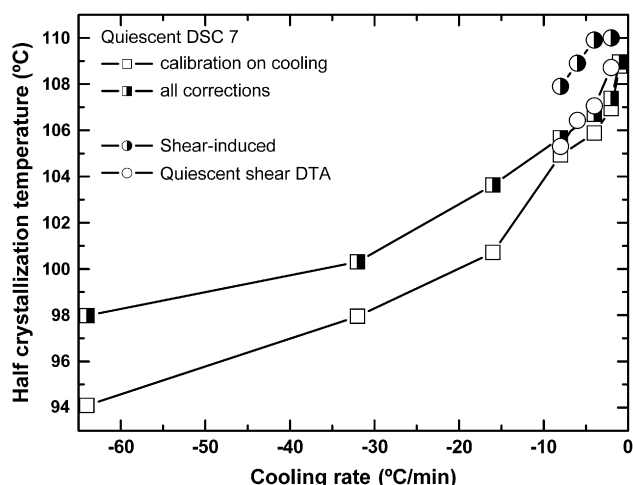


Fig. 4. Variation of the half crystallization temperature with the cooling rate. (□) and (◐) are the quiescent nonisothermal values obtained with a DSC-7. The temperature values indicated with the open squares were corrected with the calibration on cooling at each rate. The values indicated by half-filled squares contain additional corrections for the heat of crystallization released during the solidification and sample thermal resistance. The half crystallization temperature recorded with the shear DTA is also indicated for quiescent experiments (○), which include the calibration on cooling, and shear-induced crystallization experiments (●).

DSC-7 and with the shear DTA instrument, together with the values for the saturation of shear-induced nonisothermal crystallization. A shift of around ≈ 3 °C to higher temperatures is observed for the cooling rates tested. The evaluation of the memory of shear effect on the density of nuclei increase may be carried out starting from the relationship between the half crystallization time and the spherulite growth rate, assuming that the isothermal crystallization kinetics is described by the Avrami's equation and considering an instantaneous nucleation of spheres (Eq. (5) of Ref. [20]). Assuming further that in a shear-induced isothermal crystallization from a sheared melt at constant temperature, without any additional deformation applied to the supercooled melt, the spherulite growth rate is constant (because no shear flow is applied to the supercooled melt), the shift to shorter times of the half crystallization time is reflected in a higher slope of $\ln(1/t_{50\%})$ versus $1/T(\Delta T)$ with respect to the quiescent crystallization experiment at the same temperature. Therefore, for an isothermal crystallization, the ratio between the average density of nuclei for a shear-induced and quiescent experiment is:

$$\frac{\bar{N}_{sh}}{\bar{N}_q} = \exp \left\{ 3 \ln \left[\frac{(1/t_{50\%})_{sh}}{(1/t_{50\%})_q} \right] \right\}, \quad (1)$$

where the constant 3 results from the assumption of an instantaneous nucleation of spheres. For the nonisothermal crystallization experiments, the half crystallization temperature may be related to the half crystallization time, by setting the zero time at the polymer thermodynamic melting temperature. Since it was shown previously that the average density of nuclei at a certain isothermal crystallization temperature is similar to that occurring at a similar $T_{50\%}$ temperature in a nonisothermal crystallization experiment [21], based on the experimental results obtained, it may be assumed that both quiescent and shear-induced nonisothermal shear-induced crystallization experiments occur in a narrow temperature interval near the half crystallization temperature. Therefore, for each $T_{50\%}$ a corresponding half crystallization time may be evaluated. Considering the cooling rate of -8 °C/min, the shear-induced and quiescent half crystallization times are 212.15 s and 192.75 s, respectively. After substitution into the above equation it results in $\bar{N}_{sh}/\bar{N}_q \approx 1.34$, a result that was confirmed by measurements of the spherulite radius by small angle light scattering of crystallized samples. Other results were obtained for other polymers.

These results fit within current ideas of models for flow-induced crystallization. It is considered that crystallization from strained polymer melts is subjected to the thermal-induced and flow-enhanced effects, each one giving its own contribution to the crystallization rate and stored free energy [22]. The crystallization rate equation is therefore based on a nonisothermal version of Avrami's equation coupled with a term for the stored free energy of the amorphous phase that accounts for the effect of flow. The model was applied to the poly(lactic acid) crystallization evolution along a spinline and it demonstrated the above two effects. The results

obtained allowed to conclude that “crystallization, as such, is always thermally induced and if the fibre temperature is not in a range where quiescent crystallization can occur, flow-enhanced crystallization will not occur either”. This conclusion was supported by the experimental verification that crystallization only occurs after a certain distance from the spinneret (around 150 cm) where the fibre temperature has reached a value that allows quiescent crystallization to occur, although for an undeformed melt it would require a very long time.

5. Conclusions

It was shown that the effect of melt memory on shear-induced crystallization kinetics is independent of the crystallization mode, isothermal or nonisothermal. The same strain applied to the molten polymer saturates both crystallization processes, and it depends on the sheared melt temperature. Sheared melt at higher temperatures need lower strains to reach a steady state in shear flows. The steady state is the melt state responsible for the saturation of shear-induced crystallization.

The contribution of the melt memory effect to the overall nucleation density in shear-induced crystallization is small, but the understanding of its effect is important to explain the formation of precursor structures in shear flows. The results presented also indicate that thermal-induced crystallization is the major contributor to the overall density of nuclei in polymers crystallizing from sheared melts.

Acknowledgements

This research was supported by the European Community fund FEDER, through the projects POCTI//CTM/46270/2002

and PTDC/CTM/68614/2006 approved by the Portuguese Foundation of Science and Technology (FCT), which is also acknowledged for the grant BPD/5517/2001 assigned to W. Zhang.

References

- [1] Nagatake W, Takahashi T, Masubuchi Y, Takimoto JI, Koyama K. *Polymer* 2000;41:523.
- [2] Li ZM, Li LB, Shen KZ, Yang MB, Huang R. *Polymer* 2005;46:5358.
- [3] Van der Beck MHE, Peters GWM, Meijer HEH. *Macromolecules* 2006;39:1805.
- [4] Gutiérrez M-CG, Alfonso GC, Riekel C, Azzurri F. *Macromolecules* 2004;37:478.
- [5] Ryan AJ, Fairclough JPA, Terri NJ, Olmsted PD, Poon WCK. *Faraday Discuss* 1999;112:13.
- [6] Somani RH, Yang L, Hsiao BS. *Physica A* 2002;304:145.
- [7] Alfonso GC, Ziabichi A. *Colloid Polym Sci* 1995;273:317.
- [8] Ziabichi A, Alfonso GC. *Colloid Polym Sci* 1994;273:1027.
- [9] Zhang W, Martins JA. *Macromol Rapid Commun* 2006;27:1067.
- [10] Martins JA, Zhang Wd, Brito AM. *Macromolecules* 2006;39:7626.
- [11] Martins JA, Zhang Wd, Brito AM, Infante U, Romero M, Soares FO. *Rev Sci Instrum* 2005;76:105105.
- [12] Janeschitz-Kriegl H. *Colloid Polym Sci* 2003;281:1157.
- [13] Kumaraswamy G, Issaian AM, Kornfield JA. *Macromolecules* 1999;32:7537.
- [14] Bushman AC, McHugh AJ. *J Appl Polym Sci* 1997;64:2165.
- [15] Chai CK, Auzoux Q, Randrianatoandro H, Navard P, Haudin JM. *Polymer* 2003;44:773.
- [16] Nogales A, Olley RH, Mitchell GR. *Macromol Rapid Commun* 2003;24:496.
- [17] Martins JA, Zhang Wd. *Thermochim Acta* 2004;413:101.
- [18] Lavine MS, Waheed N, Rutledge GC. *Polymer* 2003;44:1771.
- [19] Smith DE, Babcock HP, Chu S. *Science* 1999;283:1724.
- [20] Martins JA, Cruz Pinto JJC. *Polymer* 2002;43:3999.
- [21] Martins JA, Cramez MC, Oliveira MJ, Crawford RJ. *J Macromol Sci Phys* 2003;42:367.
- [22] Kohler WH, Shrikhande P, McHugh AJ. *J Macromol Sci Phys* 2005;44:185.