Shear Flow Effects on Polymer Melts Crystallization: Kinetics Features

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Summary: In this work the kinetics of the isothermal crystallization from the melt of isotactic polyolefins in quiescent conditions as well as *after the application of a step-shear flow* is investigated by means of rheological measurements. It is shown that the kinetics of the crystallization, as measured by the increase of the storage modulus, is not affected by the strain amplitude and the frequency of the oscillation, once they are properly chosen.
A strong enhancement of the crystallization kinetics has been obtained when *the step-shear flow* was applied at the crystallization temperature T_C=92°C for two different molecular weight poly(1-butene) samples (i-PB400 and i-PB200) and at T_C=137°C for a polypropylene (i-PP). In particular, the overall-crystallization rate constants of the i-PB400 increased with increasing the applied shear rate at a constant total strain of 60. At higher shear flow temperatures slower kinetics occurred in all the cases until the effect of the applied shear flow was lost. Moreover, the effect of the molecular weight on the flow induced crystallization phenomenon is investigated on the two i-PB samples and the results have clearly shown that the higher molecular weight i-PB200 polymer is much more sensitive than the i-PB400 to the flow history.

Keywords: isothermal crystallization, quiescent, shear-induced, rheology, storage modulus, polypropylene, poly(1-butene).

Introduction

In most processing operations thermoplastic polymers are molten, shaped and solidified under the action of complex flow fields leading, for semi-crystalline polymers, to the phenomenon known as flow-induced crystallization (FIC) that significantly affects the overall-crystallization kinetics (1-6). Indeed, in polymer melts also a weak shear flow can accelerate the overall kinetics that is enhanced whenever crystallization appears during shear or after shear. Viscoelastic measurements have recently received considerable attention as a capable method to study the crystallization of semi-crystalline polymers either in quiescent conditions (7,8) as well as after the application of a shear flow (3, 9-11). In particular the storage modulus, G', undergoes an increase of orders of magnitude during the crystallization process because of its sensitivity to the structural changes and therefore it can monitor the crystallization from the melt to the solid state.

The transformed crystallized fraction, $\alpha(t)$, can be obtained from the time dependent $G'(t)$ values according to the equation (8):

$$\alpha(t) = \frac{G'(t) - G'_0}{G'_\infty - G'_0} \qquad (1)$$

where G'_0 and G'_∞ correspond to the G' values of the initial and final plateau, respectively. The α (t) values, ranging between 0 and 1, allow to define the half-crystallization time, $t_{0.5}$, that represents the time at which the crystallized fraction of the sample is 50%. An overall-crystallization rate constant, k, corresponding to the inverse of the half-crystallization time, can be defined from the well known Avrami equation.

In this work the storage modulus has been used as a probe to follow the crystallization process and it will be shown that the crystallization kinetics is not affected by the strain amplitude and the frequency of the oscillation, once they are properly chosen. The *quiescent* isothermal crystallization of two commercial isotactic poly(1-butene) samples of different molecular weight and of a polypropylene sample has been investigated. The results, in terms of the overall-crystallization rate constant, represent the reference condition for the study of the effect of the application of a *step-shear flow*. In these experiments the influence of the shearing temperature, T_S, the applied shear rate and the molecular weight will be analyzed and related to the relaxation behavior of the polymers.

Experimental Part

Materials and methods

In this study two isotactic poly(1-butene) samples provided by *Basel* (Louvain la Neuve), the i-PB400 and the i-PB200, and a standard isotactic polypropylene provided by *Basel* (Ferrara), the i-PPT30G, have been investigated. They are semicrystalline polymers with a melting temperature, T_m, equal to 126°C for the i-PB samples and to 165°C for the i-PPT30G. The molecular weight averages as obtained from GPC measurements by *Basel* are reported in Table1 together with the tacticity as measured by NMR C^{13} .

Sample	M_n	M_w	M_z	M_z/M_w	tacticity (%mmmm)
i-PB400	81700	244000	505000	2.1	79.5
i-PB200	107000	525000	1370000	2.6	82.7
i-PPT30G	55600	376095	1832915	4.9	87.6

Table 1. Molecular characteristics of the poly(1-butene) and polypropylene samples.

It is noteworthy that the two poly(1-butenes) samples used in this work are good candidates to investigate the effect of the kinetics enhancement in the flow induced crystallization due to the increase of the molecular weight. The i-PB200 is, indeed, characterized by the weight average molecular weight, M_w, and the z-average molecular weight, M_z, much higher than the corresponding ones of the i-PB400 sample. Moreover, the ratio M_z/M_w is quite similar for both sample showing a similar molecular weight distribution, MWD, in the high molecular weight tail; i.e. in the MWD region of interest for a flow induced crytallization point of view.

A Rheometrics RDSII rotational rheometer (*Rheometrics Inc.*), equipped with a 2÷2000 g·cm transducer, has been used for both the rheological and the crystallization experiments under nitrogen atmosphere in order to prevent the oxidation of the material.

The rheological characterization of the i-PB and i-PP melt was performed in a parallel plates geometry (∅= 25mm, gap=1mm). In the dynamic oscillatory tests the angular frequency, ω, varied from 0.1 to 500 rad·s^{-1}. The dynamic measurements have been performed at temperatures in the range 120÷190°C in the case of the poly(1-butene) samples and in the range 160÷260°C in the case of the i-PPT30G. Indeed, the rheological measurements started after the samples were annealed in the rheometer between the tools at T=160°C for 10 minutes for the i-PB and at T=240°C for 30 minutes for the i-PP samples to obtain isotropic melts. On the basis of the time-temperature superposition principle the isotherms were shifted to obtain master curves at the reference temperature of T_0=150°C and T_0=230°C for the i-PBs and i-PP polymers respectively.

Rheology of crystallization

The isothermal crystallization experiments were performed adopting a cone-and-plate configuration (∅= 25mm, cone angle= 0.1 rad). The use of the cone-and-plate guaranteed a steady simple shear flow during the application of the *step-shear flow.*

First, experiments in *quiescent* conditions have been performed and the following thermomechanical history has been adopted:

a) the i-PP samples were placed in the rheometer and kept for 30 min at 240°C; the i-PBs samples were kept between the rheometer tools for 10 minutes at 160°C. In both cases the annealing process was performed at a temperature well above the melting temperature (previously reported) to erase crystalline fragments that could affect the subsequent crystallization process;

b) the samples were, then, cooled to the crystallization temperature (T_C) with a rate of about 25°C/min. The crystallization temperatures were T_C= 135°C and 137°C for the i-PP sample, and T_C=92°C for the i-PB samples. The temperature profiles were monitored using a thermocouple in contact with the lower plate in order to minimize temperature differences between the tool and the sample. At the start of the cooling process the evolution of the storage modulus, G', was monitored versus time so that both the cooling step and the isothermal crystallization were analyzed by an oscillatory test at the constant strain amplitude of 1% and at the frequency of 1 rad/s. Indeed, the choice of the values for the strain amplitude and the frequency parameters is crucial in order to reduce as much as possible the disturbance during the crystallization process. These values also ensure that the whole crystallization process occurs in the range of sensitivity of the equipment. To verify whether these parameters could affect the crystallization kinetics, tests with frequency values ranging from 1 to 20rad/s and strain amplitude values ranging from 0.5 to 5% have been performed on the i-PB400 sample.

It is noteworthy that the storage modulus represents our probe to follow the crystallization process.

To study the *flow induced crystallization* (FIC) phenomenon, after the annealing in the melt, a *step-shear flow* at a low shear rate, $\dot{\gamma}$, was imposed during a shearing time, t_s at various temperatures, T_s, in the range between the annealing and the crystallization temperature. Then, after the flow has been stopped, the melt has been cooled at the crystallization temperature and the crystallization was recorded in **isothermal conditions** (at T_C) following G' as a function of time (as previously described). The effect of the flow on the crystallization kinetics was analyzed in terms of the overall-crystallization rate constant, k, corresponding to the reciprocal of the half time of crystallization, $t_{0.5}$.

Results and Discussion

The master curves at the reference temperature of T_0=150°C for the i-PB400 and the i-PB200 samples and at T_0=230°C for the i-PP polymer have been obtained with the time-temperature superposition principle. In Figure 1 the master curve relative to the i-PB400 is reported in terms of the elastic and loss modulus (G' and G" respectively).

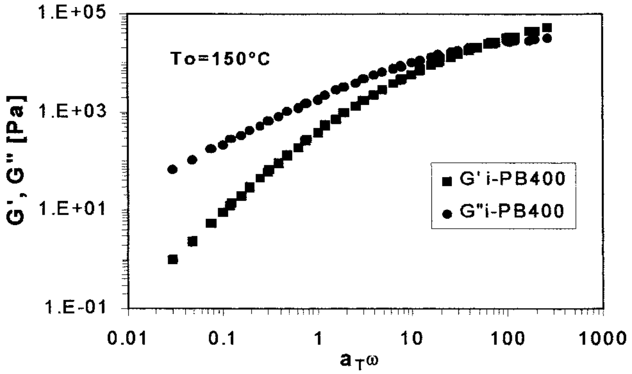

Figure 1. Master Curve of the i-PB400 at T_0=150°C.

The corresponding shift factors, a_T, are plotted vs 10^3 (1/T) (K^{-1}) and fitted with the Arrhenius expression, as shown in Figures 2a, b ,and c for the three polymers investigated.

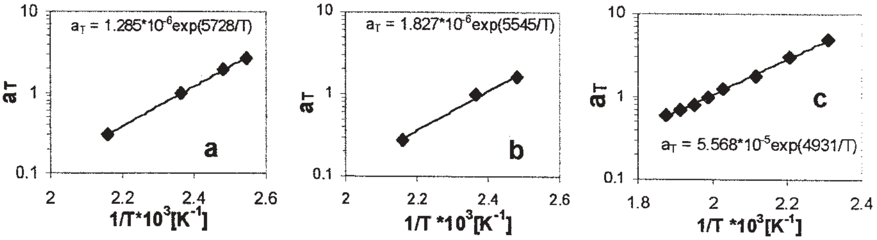

Figure 2. Shift factors a_T, vs 10^3 (1/T) (K^{-1}) for: **(a)** i-PB400; **(b)** i-PB200; **(c)** i-PPT30G.

The relationships between a_T and (1/T) (K^{-1}), reported in the Figure 2, are then used to evaluate the relaxation time spectra, H(τ), of these polymers at different temperatures (see Figures 3a, b and c) once H(τ) is calculated at the reference temperature from the master curves. To estimate the reference H(τ), first the dynamic moduli have been related to the relaxation moduli (as obtained from the GEX-double reptation modulus) using a Finite Element Approximation and then the Aury law was used. The details of the calculus of H(τ) are reported in a previous paper by Nobile and Cocchini (12). It is noteworthy that this procedure gives exactly the same H(τ) that has been more recently evaluated by Nobile and Cocchini (13) using the analytical relationship connecting the molecular weight distribution and the relaxation spectrum proposed by Thimm et al. (14)

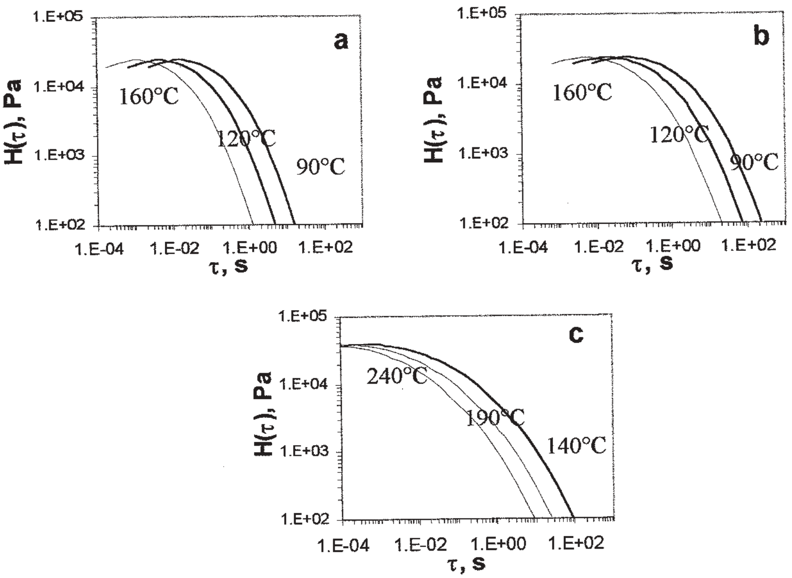

Figure 3. Relaxation time spectra, H(τ), for: **(a)** i-PB400 and **(b)** i-PB200 at T=160, 120, 90°C; **(c)** i-PPT30G at T=240, 190,140°C.

The comparison between Figures 3a and 3b shows that the i-PB200 is characterized by much longer relaxation times than the i-PB400, as expected due to its the higher molecular weight (see Table 1). This event again confirms that the two i-PB polymers chosen in this study represent good candidates for the study of the effect of molecular weight on the flow induced crystallization phenomenon since a major factor governing FIC is the relaxation behavior of the polymer chains.

Rheology of the isothermal quiescent crystallization

As previously mentioned in the Experimental section, we have first verified that the use of the storage modulus represents a reliable probe to follow the crystallization kinetics process. The analysis of the influence on the crystallization process of the applied strain amplitude has been performed on the i-PB400 sample by varying the strain amplitude values from 0.5 to 5%. The sample has been crystallized during the oscillatory measurements at Tc=92°C with a constant frequency ω=1 rad/s .

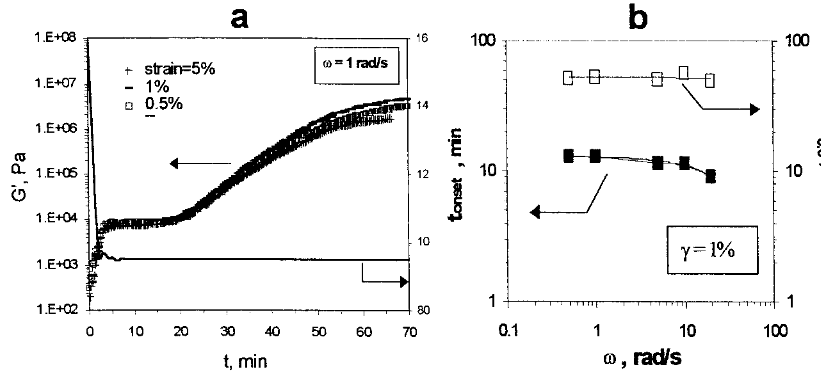

Figure 4. Quiescent crystallization of the i-PB400 at T_C=92°C monitored with oscillatory experiments. **(a)** Evolution of G' vs time applying a constant frequency (ω=1 rad/s) and different strain amplitude values (γ = 0.5÷5 %); **(b)** onset times, t_{onset}, and half crystallization times, $t_{0.5}$, evaluated from G' data, applying a constant strain amplitude (γ=1%) and different frequencies (ω=0.5÷20rad/s).

In Figure 4a the evolution of G' vs. time during both the cooling from the melt and the isothermal crystallization is reported together with the temperature profiles. After a first increase of the modulus during the cooling step, a plateau (G'_o) at T_C is observed, followed, after an instrumental onset time, t_{onset}, by a second strong growth of the modulus representative of the crystallization phenomenon and by a final plateau (G'_∞) at the end of the process. The results show that no evident effects on the crystallization kinetics of the applied strain amplitude, γ , in the range 0.5%÷5% can be detected. Therefore all the dynamic measurements reported in the following have been performed with a strain amplitude of 1%.

In Figure 4b the effect of the applied frequency is shown in terms of the onset and half-crystallization times. Again the results show that the applied frequency has no significant effect on the quiescent crystallization kinetics monitored with oscillatory tests, in the frequency range investigated. Indeed, only a slight influence on the onset time value is observed at the highest frequencies. The frequency of 1 rad/s has been, then, chosen to perform all the crystallization experiments.

Rheology of the isothermal crystallization after a step-shear flow

The influence of the *step-shear flow* applied at different temperatures, T_s, on the overall crystallization kinetics has been investigated for the i-PB200 and i-PB400 polymers at Tc=92°C. The results are reported in Figure 5 in terms of the ratio between the overall-crystallization rate constant as measured in the G' crystallization experiments *after the step-shear flow*, k_S, and the corresponding value of the quiescent experiment, k_0. The quiescent experiment is, indeed, our reference condition and the effect of the *step-shear flow* on the crystallization kinetics will be always reported in comparison to the quiescent case.

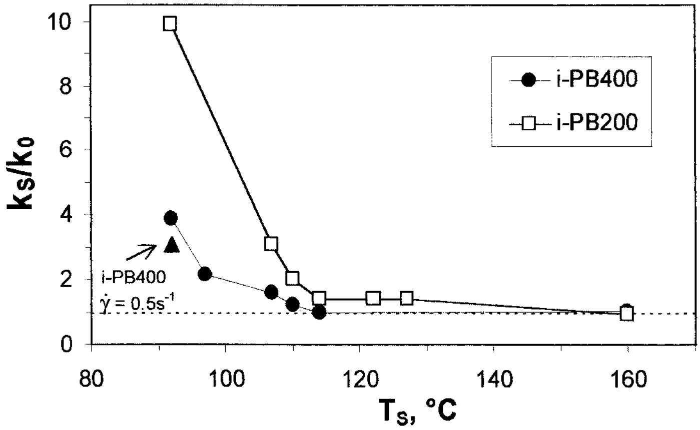

Figure 5. The effect of the shearing temperature on the overall crystallization rate at Tc=92°C for the i-PB200 sample (shearing conditions: $\dot{\gamma}=0.5s^{-1}$, $\gamma=60$) [open squares] and i-PB400 sample (shearing conditions: $\dot{\gamma}=1s^{-1}$, $\gamma=60$ [full circles] and $\dot{\gamma}=0.5s^{-1}$, $\gamma=60$ [full triangle]).

When a *step-shear flow* with the shear rate of 1 s^{-1} and γ= 60 is applied to the i-PB400 at the crystallization temperature of 92°C the overall isothermal crystallization kinetics is strongly accelerated, i.e. the k_S/k_O is 3.9. Increasing the temperature at which the shear flow is applied, T_s, from 92°C to 114°C, slower kinetics occur. For T_s higher than 114°C the effect of the applied shear flow is lost (i.e. the ratio k_S/k_O becomes 1).

These results clearly show that a major factor governing the flow induced crystallization phenomenon is the relaxation behavior of the polymer chains. Indeed, the relaxation spectrum of the i-PB400 polymer, reported in Figure 3a, shows a significant increase of the longer relaxation times with decreasing the temperature from 160°C to 90°C. In the case of the higher molecular weight sample, the i-PB200, the effect of *the step-shear flow* has been investigated at the shear rate of 0.5 s^{-1} that was the highest possible shear rate at the lower T_s used (due to the transducer limit). Also in this case a total strain, γ, equal to 60 was adopted for all the experiments. Again, the effect of the applied shear flow vanishes increasing the temperature T_s.

A strong influence of the molecular weight on the FIC, as expected, is evident from our results. Indeed, in order to compare exactly the same shear flow condition, the result for the shear flow applied to the i-PB400 at Tc=92°C with a $\dot{\gamma}= 0.5s^{-1}$ and γ=60 is also reported in Figure 5. The k_S/k_O value for the i-PB400 is 3.1 and for the i-PB200 is 9.9 showing that the higher M_w sample is much more sensitive to the shear flow history, as also clearly reported in the works by Somani *et a.l* (4) and by Jay *et al.* (6). Again, this results can be justified in terms of the relaxation behavior of the polymers. The relaxation spectra of the i-PB200 sample (Figure 3b) are, in fact, characterized by relaxation times much longer than the corresponding ones of the i-PB400 (Figure 3a).

To investigate the effect of the applied shear rate, step-shear flow experiments have been performed on the i-PB400 sample at the crystallization temperature of 92°C with shear rates ranging between 0.25 and 5 s^{-1} and a constant total strain γ= 60. In Figure 6a the results for two tests at $\dot{\gamma}=0.25s^{-1}$ and $\dot{\gamma}=5s^{-1}$ are reported in terms of G' vs. time together with the results for the quiescent crystallization. A very good reproducibility is obtained in all the rheological crystallization experiments. The results of the analysis of the applied shear rate in the whole range investigated is shown in Figure 6b in terms of the overall-crystallization rate ratio, k_S/k_O.

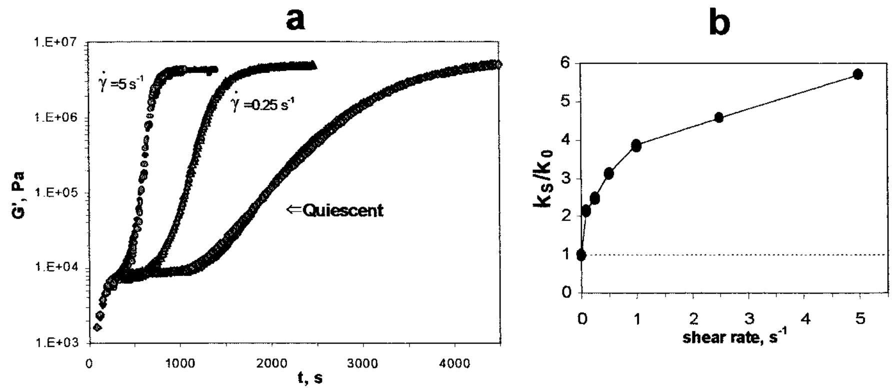

Figure 6. Shear rate effects for the i-PB400 crystallized at T_C= 92°C after a *step-shear flow* at T_S= 92°C and γ = 60: **(a)** G' vs time after the *step-shear flow* for two tests with $\dot{\gamma}$=0.25, two tests with $\dot{\gamma}$=5 s^{-1} and two tests for the quiescent crystallization kinetics; **(b)** k_S/k_O vs the shear rate in the range $\dot{\gamma}$=0.1÷5 s^{-1} investigated.

At a fixed shear deformation, the higher is the applied shear rate, the faster the crystallization occurs after the flow has been stopped.

In Figure 7 the results of the study of the *flow induced crystallization* of the i-PPT30G with different shear rates, $\dot{\gamma}$= 1, 2.5 and 5 s^{-1} at the same total deformation of γ=1000 are reported.

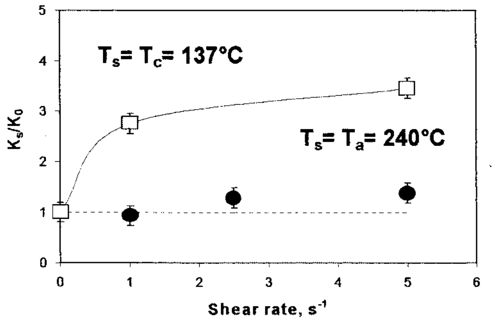

Figure 7. Effect of the shear rate on the crystallization rate constant of the i-PP T30G. Filled symbols: shearing temperature, T_s= 240°C; shearing deformation, γ=1000; crystallization temperature, T_c = 135°C. Open symbols: T_s=T_c=137°C, γ =200.

It is possible to observe that a *step-shear flow* imposed in the melt at the shearing temperature

T_S= 240°C (filled circles in Figure 7) has a very low effect on the subsequent crystallization kinetics: the ratio between the sheared and the quiescent overall-crystallization rate constants, k_S/k_O, does not exceed 1.4 , even if the applied strain, γ =1000, is quite high. In order to produce stronger effects the shear flow must be imposed at much lower temperatures, *e.g.* at the crystallization temperature (T_C=137°C). In these conditions the shear flow is highly effective and the overall-crystallization rate constant is seen to increase, at constant shear deformation, with increasing the shear rate (open squares in Figure 7).

Conclusions

In this work the *quiescent* isothermal crystallization of two different molecular weight isotactic poly(1-butene) polymers and of an isotactic polypropylene sample, as well as the crystallization *after the application of a step-shear flow*, has been studied by means of rheological measurements. In particular, it was shown that the kinetics of the crystallization as measured by the increase of the storage modulus is not affected by the strain amplitude and the frequency of the oscillation, once they are properly chosen.

A strong enhancement of the crystallization kinetics has been obtained for all the samples when *the step-shear flow* was applied at the crystallization temperature. In particular, the overall-crystallization rate constants increased with increasing the shear rate applied at a constant total strain of 60. At higher shear flow temperatures slower kinetics occurred until the effect of the applied shear flow was lost. Moreover, the results have shown that the higher molecular weight i-PB200 polymer is much more sensitive to the flow history than the i-PB400. These results clearly show that a major factor governing the flow induced crystallization phenomenon is the relaxation behavior of the polymer chains.

Acknowledgments

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