Flow-induced crystallization in poly-1-butene: the shish-kebab transition

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ABSTRACT: In this work, flow-birefringence measurements have been performed to monitor the orientation development during application of high shear flow in undercooled polymer melts. It is demonstrated that a critical shear rate and a critical shear strain are required in order to form strongly oriented shish-kebab structures. After reaching such critical conditions, the crystallization kinetics – measured both by means of birefringence as well as transmitted intensity measurements – is drastically increased. The results generated in this work suggest that Janeschitz-Kriegl's [1] hypothesis about the need for a specific amount of work required to form shish-kebab structures is valid, at least for the conditions investigated.

Key words: Flow-induced crystallization, Birefringence, Shish-kebab, Critical work

1 INTRODUCTION

The majority of polymers are semi-crystalline and inevitably, these crystals are oriented by flow during processing. The morphology of semi-crystalline polymers strongly affects their physical properties. In order to optimize these properties, an understanding needs to be developed on how flow-induced orientation competes with crystallization. At high processing speeds, profound changes in crystalline structure and properties are associated with the flow-induced transition from a relatively isotropic, spherulitic morphology to a highly oriented, shish-kebab morphology. The latter structures lead to a massive increase in stiffness and in strength.

2 EXPERIMENTAL SECTION

2.1 Materials

The isotactic PB-1 (PB0400) used in this study is a commercial grade provided by Basell Polyolefins in the form of pellets. It has an isotacticity of 98.8% and contains no nucleating agents. PB0400 has a M_w = 176 kg/mol and a polydispersity of 5.7 (data obtained from GPC measurements by Basell Polyolefins). More material properties and a rheological characterization of PB0400 can be found in previous publications [2, 3].

2.2 Methods

For the experiments, a shear cell [3, 4] developed at the Solvay Central Laboratory was used. It is a small sandwich type cell in which the sample is uniaxially sheared between two oppositely moving glass windows, driven by a servomotor. The glass windows of the cell are incorporated in sample holders which are placed in independently heated conditioning blocks. The typical thickness of a sheared sample is 50-100 µm. The shear cell can be operated from the low shear rate region up to rates of 1500 s^{-1} and deformations up to a few hundred shear units can be achieved. The main advantage of this shear cell is that the probed structure is homogeneous, i.e. there is a constant shear rate throughout the entire sample, which is not the case for the extrusion die configurations that have been used previously (see for instance [5, 6]).

Windows and holes are provided in the equipment to view the flow-vorticity plane of the sheared sample. An optical train consisting of a modulated laser allows to follow the transmitted intensity I_{dc} and the birefringence $\Delta n'$ during shear flow and subsequent crystallization. The birefringence during shear is related to the anisotropy in the conformation of polymer chains, whereas the transmitted intensity and the birefringence after the onset of crystallization arise due to scattering from crystallites and are sensitive to the size, shape and anisotropy of the crystallites.

To erase the thermal and flow history, the samples were always annealed at 200°C for 10 minutes in a separate oven. Subsequently they were cooled to 150°C and transferred to the conditioning blocks kept at the desired crystallization temperature T_c. This procedure avoids long cooling times typical of the already mentioned extrusion die configurations (e.g. [5, 6]). The thermal characteristics of the setup resulted in a time of about 10 minutes to quench the sample to the measurement temperature. For the experiments, zero time scale was assigned to the start of the shear flow, corresponding to the instant at which the crystallization temperature T_c was reached. In all the experiments the transmitted laser light was measured during shear flow and subsequent isothermal crystallization.

More details on the construction, the temperature control and the limitations of the shear cell, the optical setup and the calculation of the birefringence can be found in references [3, 4].

3 RESULTS AND DISCUSSION

3.1 Detection of the shish-kebab transition

The use of the sandwich type shear cell in combination with the optical setup described in the previous section, provides different ways to detect the formation of the highly anisotropic shish-kebab structure [3, 4].

A first indication is the presence of an unusual upturn in the flow birefringence. In their extrusion die experiments, Kumaraswamy et al. [5, 6] pointed out the presence of such an upturn above a critical shear stress and strain and attributed this to a change in the crystallization mechanism, i.e. the formation of a ‘shear-induced structure’ related to the presence of oriented precursors. A similar upturn was observed at high shear rates for experiments on i-PP [4] and PB-1 [3] using a sandwich type cell. In figure 1, the birefringence of PB0400 during the short flow pulse is plotted for different shear rates $\dot{\gamma}$ (T_c=98°C and γ=100). The instant at which the shear flow is stopped is indicated by circles. The curves show the typical behavior previously described in literature [3-6]: a slight overshoot stabilizing to a plateau level (related to the level of molecular orientation), followed by a relaxation. However, for the highest shear rate shown, $\dot{\gamma}$=462 s^{-1}, there is an unusual upturn in the flow birefringence curve and the birefringence hardly relaxes after cessation of flow, indicating the formation of shish-kebab structures.

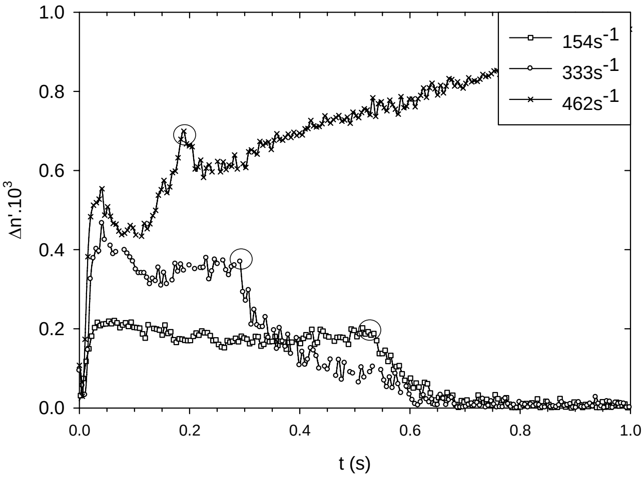

Figure 1. Flow birefringence of PB0400 (T_c=98°C and γ=100). Circles indicate the end of each shear pulse.

A second indication for the formation of the shish-kebab structure is the sharp increase in the crystallization kinetics. To qualitatively determine the crystallization kinetics, the time needed to reach 50% of the maximum of the birefringence, defined as $t_{0.5}$, and the instant for which the transmitted intensity reaches its minimum, defined as t_{min}, were used. In figure 2 both characteristic time scales, $t_{0.5}$ and t_{min}, are plotted as a function of the shear rate for the crystallization of PB0400 (T_c=98°C and γ=100). As was shown in previous studies [3, 4], there is a good quantitative agreement between both crystallization times. The obvious change in the slope of these curves at higher shear rates corresponds to the characteristic upturn in flow birefringence (for which the presence is indicated by grey symbols in figure 2), and thus with the onset of the highly anisotropic structure formation.

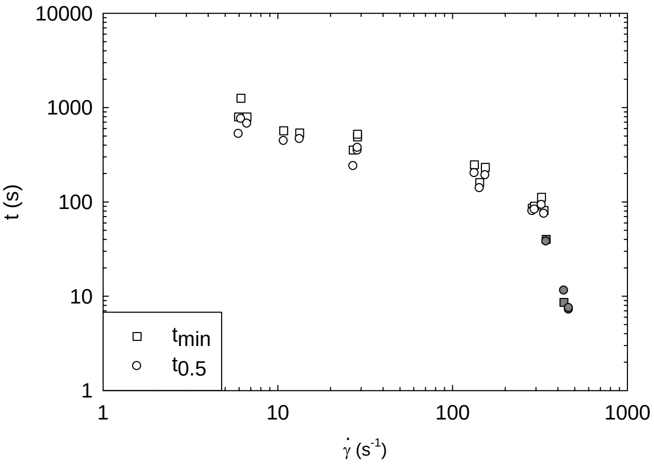

Figure 2. Characteristic time scales as a function of shear rate for the crystallization of PB0400 (T_c=98°C and γ=100). The presence of the characteristic upturn in the flow birefringence is indicated by grey symbols.

From figures 1 and 2 it can be concluded that there exists a critical shear rate required for the formation of the shish-kebab structure.

However, it can be shown that a high shear rate only is not enough to attain the transition to shear-induced structures. In figure 3, the characteristic crystallization time $t_{0.5}$ of PB0400 is plotted as a function of shear strain for two different shear rates (T_c=103°C).

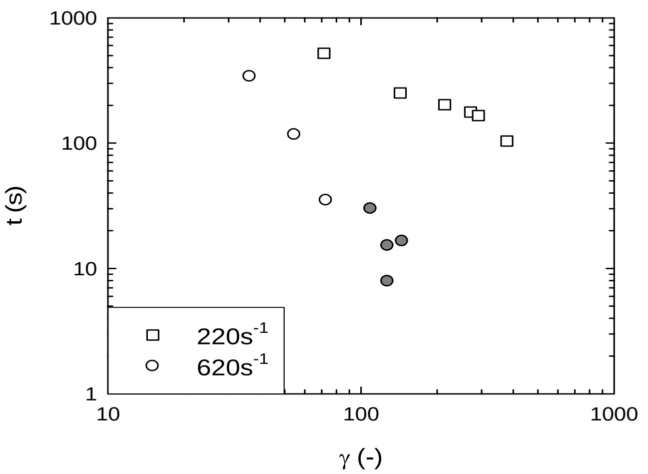

Figure 3. Crystallization time $t_{0.5}$ of PB0400 as a function of shear strain for two different shear rates (T_c=103°C). The presence of the characteristic upturn in the flow birefringence is indicated by grey symbols.

For the lowest shear rate, $\dot{\gamma}$=220s^{-1}, the transition to shear-induced structures, characterized by a sharp decrease in crystallization time, could not be attained within the experimental limits of the shear cell. For a shear rate $\dot{\gamma}$=620s^{-1} however, this transition is observed, again corresponding to the characteristic upturn in the flow birefringence (grey symbols).

The above observation suggests that the shear rate also has to be applied for a sufficiently long time. In other words: a critical shear strain exists. From figure 3 it can also be seen that the critical shear strain necessary to attain a transition to shear-induced structures decreases with increasing shear rate and that, for a larger shear rate, shear strain has a more pronounced influence on crystallization kinetics as indicated by the steeper slope of the curve formed by the data points at $\dot{\gamma}$=620s^{-1}.

The existence of a critical shear strain already indicates that the critical shear rate is not a universal parameter for the formation of shish-kebab structures. This is discussed in more detail in the following section.

3.2 Specific work as a critical shear parameter

In figure 4 the critical shear-rate for the formation of shish-kebab structures is plotted against flow time for different series of flow-induced crystallization experiments of PB0400. The lines connecting datapoints indicate the uncertainty interval for the observed transition to shish-kebabs. The fact that this critical value falls off with increasing flow time, points towards a total amount of flow being an important criterion and suggests Janeschitz-Kriegl's hypothesis [1] that there is a specific amount of work (energy density in MPa = J/cm^{-3}) required to form shish-kebabs.

The specific mechanical work, w, is obtained from the integral of the product viscosity, η, and the square of the strain rate over the total shearing time, t_s:

$$w = \int_0^{t_s} \eta(\dot{\gamma}, T)\dot{\gamma}^2(t)dt \quad (1)$$

For the 'constant-shear' experiments in this study the specific work can simply be calculated as:

$$w = \eta(\dot{\gamma}, T)\dot{\gamma}^2 t_s = \eta(\dot{\gamma}, T)\dot{\gamma}\gamma \quad (2)$$

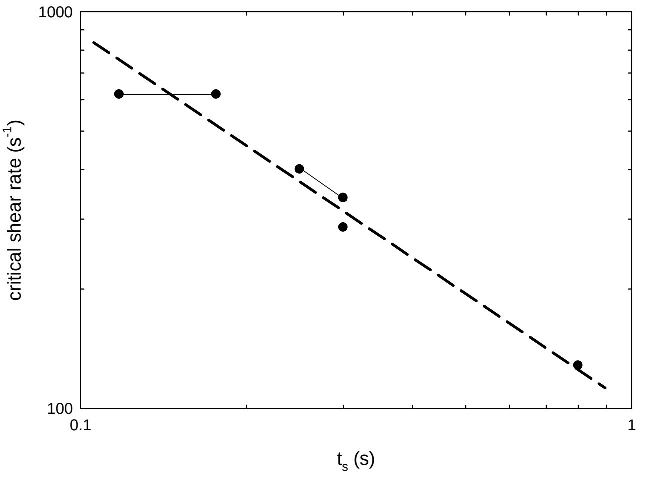

Figure 4. Measured critical shear rates required for the formation of shish-kebabs versus shearing time for the flow-induced crystallization of PB0400 (γ =100). The dashed line is added for clarity.

In figure 5, the specific work is plotted versus the critical shear rate required for the formation of shish-kebabs. It clearly shows that oriented structures only form if more than a certain amount of work has been performed on the melt. For PB0400 this critical specific work is about 9 MPa, as indicated by the dashed line in figure 5.

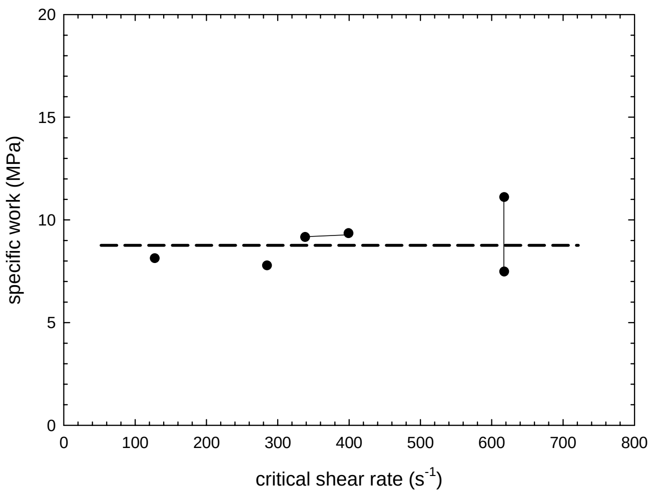

Figure 5. Specific work versus measured critical shear rates required for the formation of shish-kebabs in the sheared PB0400 (γ =100). The dashed line corresponding to the critical specific work is added for clarity.

It has been found that the criterion of a specific work to form shish-kebab crystals applies equally well to other polymers. However, the magnitude of the specific work required to create shish-kebab structure will depend on the chemical structure of the polymer.

4 CONCLUSIONS

The use of a sandwich type shear cell in combination with optical techniques allows for an accurate determination of the transition to highly oriented shish-kebabs in flow-induced crystallization of an isotactic PB-1. This transition is characterized by both a characteristic upturn in the birefringence during flow, and a sharp increase in the crystallization kinetics as obtained from characteristic crystallization times. Results confirm that the shish-kebab structures only form if more than a certain amount of work has been performed on the melt.

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