Approaching processing conditions with classical rheometrical flows

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ABSTRACT

During processing, polymers are subjected to rather severe thermo-mechanical histories. In this paper, examples will be demonstrated on how classical rheometrical flows can be used to obtain information on the processing behaviour. As an example, flow-induced crystallization of particle-filled poly-propylene will be investigated using a sliding plate rheometer that allows to cover shear rates and shear strains that are closely related to processing conditions.

INTRODUCTION

During the past decades, many different rheometers have been developed, each of them with their own advantages and drawbacks. Despite the many differences amongst all these machines, the main goal has always been to characterize the material as good as possible and at conditions as close as possible to real-life processing conditions. For instance, in the field of flow-induced crystallization, one is of course interested in obtaining insight in the relation between flow conditions, the kinetics of crystallization and the final resulting morphology. Since the seminal work of Lagasse and Maxwell[1], many studies have been devoted to this topic[2]. Many of them use real processing flows to study this problem. However, whereas these flows are close to reality, it remains difficult to isolate the effect of flow because of the occurrence of thermal and flow gradients. On the other hand, many flow-induced crystallization studies use well-defined rheometrical flows with controlled thermal and flow conditions. However, the drawback of this approach is that it becomes difficult to attain strains and strain rates that are characteristic of a processing operation. In this work, an attempt is made to bridge the gap by using rheometrical flows to attain high flow rates. As an example, results on the flow-induced crystallization of particle-filled polypropylene will be demonstrated.

MATERIALS AND METHODS

To demonstrate the effect of particle shape on the flow-induced crystallization of polypropylene, home-made hematite particles with different anisotropies have been used. Hematite has been chosen since the surface properties, important for the interaction with the polymer, can be controlled accurately. Hence, particles with different shapes but with identical interactions with the polymer can be synthesized.

The flow cell used in this work consists of a parallel plate geometry, equipped with a robust temperature control unit. The use of such a cell ensures a simple shear flow and by changing the gap thickness, shear rates and shear strains can be varied up to values

of respectively 1000 s^{-1}. The crystallization is followed on-line by means of birefringence measurements. This in-situ and time-resolved technique is able to characterize the amount of orientation in the material and to obtain information about the kinetics of the crystallization process. Details of the cell can be found elsewhere[3,4].

The experimental protocol used in this work is the so-called 'short term shearing protocol' originally introduced by the group of Janeschitz-Kriegl[5]. It consists of bringing the material above the melting temperature in order to erase the thermo-mechanical history. Subsequently, the material is cooled to a certain crystallization temperature. When this temperature is reached, a shear step is applied using the shear rate and the shear time as variables. By using this approach, temperature and flow effects can be separated.

RESULTS AND DISCUSSION

The optical methodology used in this work has the advantage that it can follow the molecular dynamics during and after the application of flow. A typical example for the unfilled polypropylene is shown in figure 1. In this figure, different shear rates have been applied but the total shear strain has been kept constant. For instance, when applying a shear rate of 94 s^{-1}, it is seen that the birefringence increases towards a plateau value, characteristic of the induction of molecular orientation. When flow is removed, this orientation relaxes. However, when the shear rate becomes sufficiently high (e.g. 255 s^{-1}), it is seen that even during flow, an upturn is observed in the birefringence. This upturn has been shown to result from oriented structures that finally will lead to a shish-kebab morphology[4,6,7].

In figure 2, the birefringence for the same experiment is shown but now for times after cessation of flow. From figure 2, interesting conclusions can be derived.

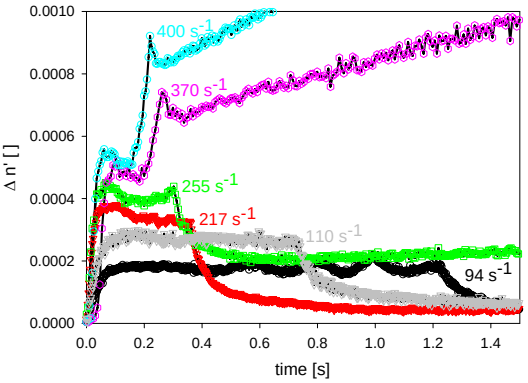

Figure 1: Birefringence evolution during the application of flow (different shear rates, strain=100, 145°C)

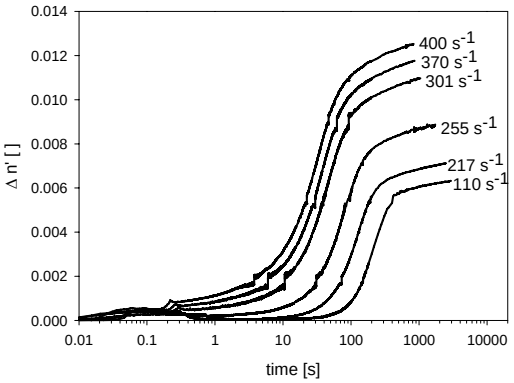

Figure 2: evolution of the birefringence after cessation of flow (different shear rates, strain=100, 145°C)

First, it can be seen that, as expected, the kinetics of the crystallization process is significantly increased when the shear rates becomes larger. Secondly, when the flow intensity is increased, the final value of the birefringence also increases which points to a higher degree of orientation. From the birefringence curves of figure 2, characteristic crystallization times can be defined. Here, the inflection point of the curves is taken as a characteristic value.

The effect of particle anisotropy on the flow-induced crystallization can be summarized in figure 3. Here, the characteristic crystallization times as defined above are plotted as a function of the applied shear rate. In this graph, three

different particle shapes have been used: spherical hematite particles (AR 1) and two other anisotropies (1.8 and 3.6).

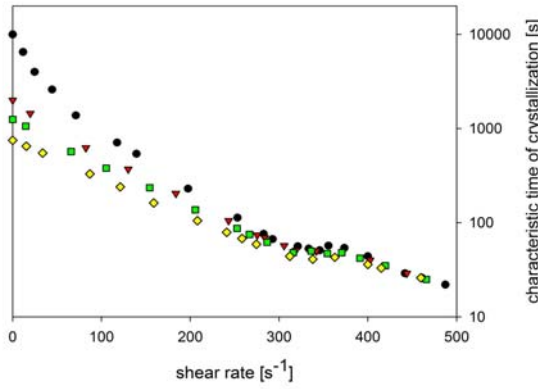

figure 3: Characteristic times as a function of shear rate (circles: neat polymer, triangles particles with aspect ratio 1, squares aspect ratio 1.8 and diamonds aspect ratio 3.6).

From the graph, it is clear that at low shear rates, the particles have a clear nucleating ability. For instance, when comparing the neat polymer with the polymer containing hematite particles with aspect ratio of 3.6, it is clear that the characteristic crystallization time differs with almost one decade. However, when shear rate is increased, the difference in crystallization kinetics between the different materials becomes insignificant and flow starts to dominate the nucleation efficiency. The latter observation was also made by for instance D'Haese et al.[8], in which the effect of particles size on flow-induced crystallization was discussed. At low values of the shear rate, particle size greatly influenced crystallization dynamics whereas at high values of the flow intensity, the applied flow field dominated the crystallization kinetics. From these data, it is clear that orientation effects, induced by flow, are indeed a very effective route to nucleate polymers, a method that is proven to be even more efficient that heterogeneities present in the material.

ACKNOWLEDGMENTS

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