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ORIGINAL PAPER

Experiments and analysis of stress-induced stiffening of a polypropylene

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ABSTRACT

Describing the solidification process is very important in polymer processing. In polypropylene (PP), the increase of viscosity, named stiffening or hardening, is determined by a rise in crystallinity. When PP flows in a channel or is stretched on a chill roll, the stress induces an anticipated crystallization and thus can lead to an unexpected solidification. This study explores how flow fields influence the crystallization behavior of PP. A controlled-stress rheometer was used to investigate the effect of short shear stress steps on crystallization kinetics. The results revealed that applying a stress step significantly increased the rate of crystallization compared to a non-stressed sample. This acceleration is attributed to the stress-induced orientation of macromolecules, which promotes nucleation. Furthermore, longer durations of applied stress led to a faster increase in viscosity, indicating a higher nucleation density with increasing stress exposure. A mastercurve approach validated the consistency of the model describing the stress-crystallization relationship. The calculated parameter relating to nucleation density confirmed a linear increase with stress duration, allowing estimation of the nucleation rate during shear. **Polyolefins J (2024) 11: 149-154**

Keywords: Polypropylene; rheology; nucleation rate; crystallization.

INTRODUCTION

Polypropylene is one of the most used polymers for a vast field of applications due to its unique properties [1-3]: low cost, low density, good mechanical properties, high durability. Polypropylene can be processed by injection molding [4] and film casting [5]. In both processes, the polymer solidifies while it is subjected to intense flow-fields: in injection molding, the melt flows very quickly in narrow cold channels [6], and in film casting the melt is drawn by the chilling rolls where it solidifies [7]. During this cooling phases, the polymer crystallizes, with dramatic effects on density [8], specific heat and conductivity [9], mechanical and optical properties [10-13] and rheological parameters [14-16]. The effect of crystallinity on viscosity is particularly significant for processing, and the increase of viscosity due to crystallization can cause an anticipated solidification [17-19]. The crystallization of polypropylene is a phenomenon strongly depending on the thermomechanical environment in which it takes place [20-22]. The most important parameter

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that determines the phenomenon is temperature, which affects the crystallization kinetics, which is usually described by a bell-shaped curve [23]: the crystallization is very slow at temperature close to the melting point and at temperature close to the glass transition, and faster at intermediate temperatures [24,25]. Another significant parameter is pressure, which normally causes an increase of the relevant temperatures [26-28] and consequently affects the kinetics of crystallization [12,26]. When the polymers crystallize under a flow field, a third parameter must be considered, namely the strain which orients the macromolecules and thus increases the crystallization kinetics [27,29]. The effect of stress on crystallinity of polymer and its significance in polymer processing has been studied by several methods in the literature [30-32]. The most adopted methods include the measurement of the evolution of rheological parameters during [33] and after [34] flow. In this work, the evolution of shear viscosity after short steps of shear stress is used as a method to assess the effect of stress on the crystallization of a polypropylene.

EXPERIMENTAL

material

The material used in this work is a commercial grade of polypropylene produced by Lyondell Basell with the trade name Hostalen PP H1850. This is a high viscosity resin, with melt flow rate of 1.2 g/10 min suitable for injection molding of parts with demanding mechanical requirements. The main properties of the resin are summarized in Table 1 according to the technical data sheet.

A TA Instruments CSL 100 controlled-stress rheometer was used to carry out rheological measurements. A parallel plates geometry with a plate diameter of 25mm was used. The viscosity of the polymer was measured at three different temperatures, 140°C, 170°C and 200°C, in dynamic mode in the frequency range from 0.1 to 100 rad/s.

Table 1. Main properties of Hostalen PP H1850.

Physical Property	Standard	Value
Melt flow rate at 230°C/2.16 kg	ISO 1113	1.2 g/10 min
Density	ISO 1183	0.90 g/cm^3
Tensile Modulus	ISO 527	1300 MPa
Tensile Stress-at-Yield	ISO 527	33 MPa
Elongation-at-Yield	ISO 527	14%
Charpy Impact Strength N, 23°C	ISO 179	16 kJ/m^2
Heat Deflection Temp. B (045MPa Unannealed)	ISO 75B	95°C
Vicat Softening Point (A50), 9.81N	ISO 306	155°C

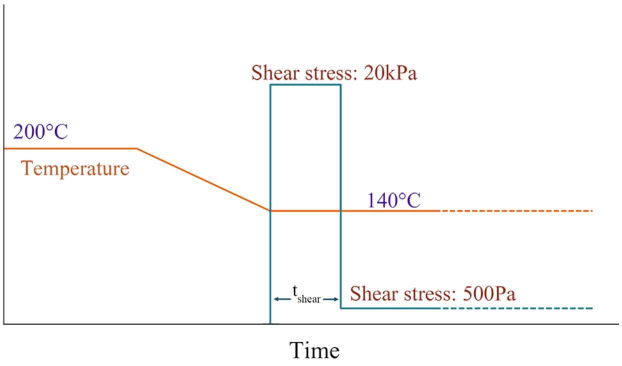

Figure 1. Protocol of temperature and stress applied during the test.

The effect of flow on crystallization kinetics was assessed by a step shear protocol. The pellets of polymer were loaded between the two plates of the rheometer at 200°C and the gap was adjusted to 1.2 mm. The polymer was then cooled down to 140°C at a cooling rate of about 5°C/min and the gap was finally adjusted to 1mm before taking out the extra material and starting the test. The test started with a step in which the shear of 20 kPa, corresponding to a shear rate of about 1 s^{-1}, was set in continuous rotation mode. Different times were chosen for the step: 0 s (namely a test without shear), 5 s, 10 s, 20 s and 40 s. The test at 40 s was repeated twice to assess the reproducibility. After the step, a stress of 500 Pa (corresponding to a shear rate of about 0.01 s^{-1}) was applied to monitor the viscosity evolution with time. The test was interrupted when the viscosity reached a value about 20 times larger than the starting value after the shear step. The protocol adopted is reported in Figure 1.

RESULTS AND DISCUSSION

Experimental results

The results of the rheological tests are illustrated in Figure 1 as symbols. The viscosity plots exhibit the typical characteristics of thermoplastic polymers, with a negative slope on a log-log plot, which decreases as the frequency increases. As expected, the viscosity decreases as the temperature increases.

Assuming the validity of the Cox-Merz rule for polypropylene, it is possible to find a relationship between shear rate and shear stress for the amorphous melt. This relationship is reported in Figure 3, from which it is clear

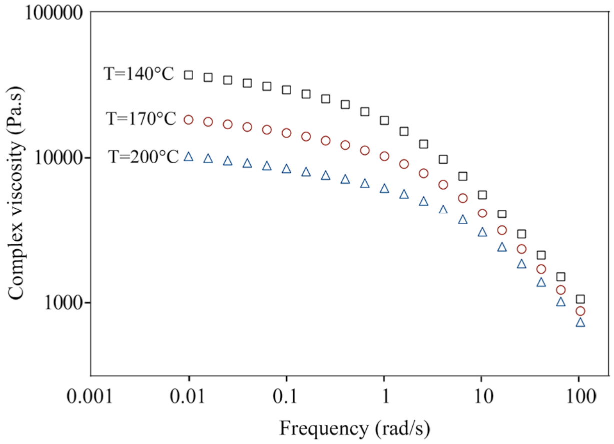

Figure 2. Viscosity of polypropylene as a function of frequency.

that the shear rate obtained during the stress stage at 20 kPa is about 1 s^{-1} and the shear rate obtained immediately after the shear stage is about 0.01 s^{-1}.

The viscosity measured after the shear step is reported in Figure 4. The data are normalized with respect to the value of the viscosity measured soon after the shear step. It is important to notice that the viscosity measured before applying the shear step is the same measured after the end of the step.

The results reported in Figure 4 show that after a time which depends on the duration of the shear stress step the viscosity starts to increase. For the test without step at high stress, the viscosity increases after about 2.5 h. The times are significantly shorter for the test in which high stress is applied and decrease on increasing the duration of the stress, so that for the test in which the shear step lasted 40 s the increase of viscosity starts after about 1h.

The increase of viscosity is related to the increase of crystallinity, according to the phenomenon which is named hardening [35] or stiffening in the literature [14].

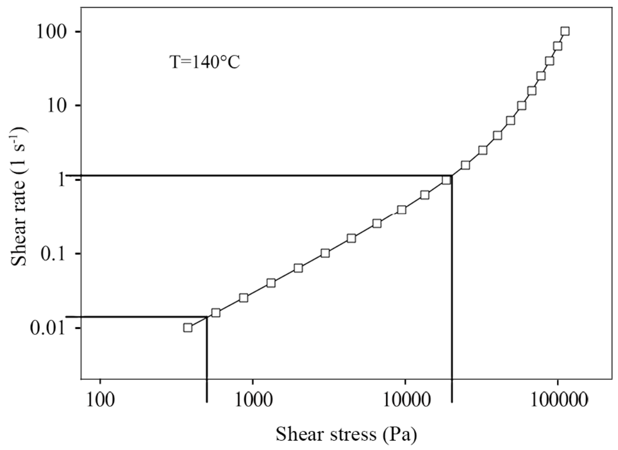

Figure 3. Relationship between shear rate and shear stress for amorphous polymer.

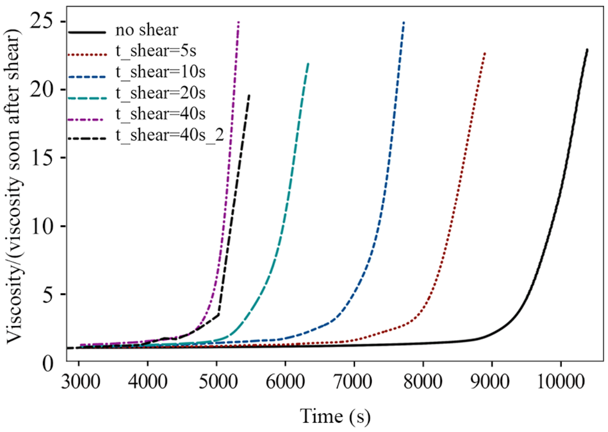

Figure 4. Viscosity of polypropylene during time after the shear step. The test at 40s was repeated twice to assess the reproducibility.

Analysis of results

The description of the increase of viscosity by effect of crystallization can be expressed by the following equation [35,36]:

$$\eta\left(T,\dot{\gamma},\alpha\right)=\eta\left(T,\dot{\gamma},\alpha=0\right)exp\left(a\alpha^{b}\right) \tag{1}$$

where T is the temperature, $\dot{\gamma}$ is the shear rate, α the crystallinity degree and a and b are constant parameters.

It can be assumed that the crystallinity evolution can be described by the Kolmogorov equation [37]:

$$\alpha=1-exp\left(-\frac{4\pi}{3}\int_{0}^{t}\dot{N}\left(s\right)\left[\int_{s}^{t}G\left(u\right)du\right]^{3}ds\right) \tag{2}$$

where $\dot{N}$ is the nucleation rate and G the growth rate of the spherulitic structures.

The nucleation rate of polypropylene is a function of the stress: it is nearly zero at low stress levels, namely when the flow is not strong enough to induce orientation [38], and it is constant if the stress is constant [39]. The growth rate is normally assumed to be a function of temperature. The evolution of crystallinity after the shear step, namely in nearly quiescent and isothermal conditions, can be thus expressed as:

$$\alpha=1-exp\left(-\frac{4\pi}{3}N_{s}G^{3}t^{3}\right) \tag{3}$$

where N_s is the nucleation density reached at the end of the shear step.

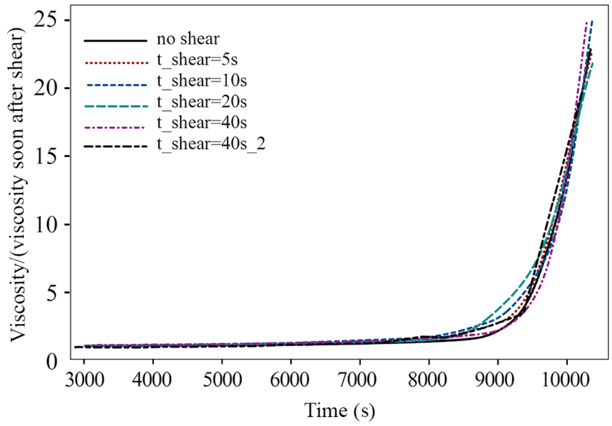

Figure 5. Mastercurve of the results reported in Figure 4, when time is shifted by the parameter ks depending on the test.

On the basis of Eqs 3 and 1 it can be stated that the results reported in Figure 4 should collapse on a single mastercurve when reported versus $k_s t$, in which k_s is a constant, which is different for each test and given by:

$$k_s = \sqrt[3]{\frac{N_s}{N_{s0}}} \tag{4}$$

where N_{s0} is the nucleation density of the sample when no shear stress is applied (quiescent).

This procedure is applied to obtain Figure 5. It can be noticed that indeed a mastercurve can be obtained if a suitable parameter k_s is chosen for each test.

The values of the parameter k_s for each test are reported in Table 2.

According to Eq. 4, the cube of the parameter k_s is the nucleation density at the end of the stress shear step. The nucleation density versus the duration of the stress shear is reported in Figure 6. It can be noticed that the slope is linear. This suggests that indeed the nucleation rate during the shear is a constant, and also allows to calculate its value as 0.152. Eq. 5 describes the effect of time on the nucleation density during a stress shear step of 20 kPa, corresponding to about 1 s^{-1} of shear rate. The nucleation rate during the step is given by Eq. 6.

Table 2. Values of the parameter k_s to obtain the mastercurve reported in Figure 5.

Duration of shear stress step in s	k_s
0	1
5	1.17
10	1.35
20	1.65
40	1.95
40 (2nd test)	1.88

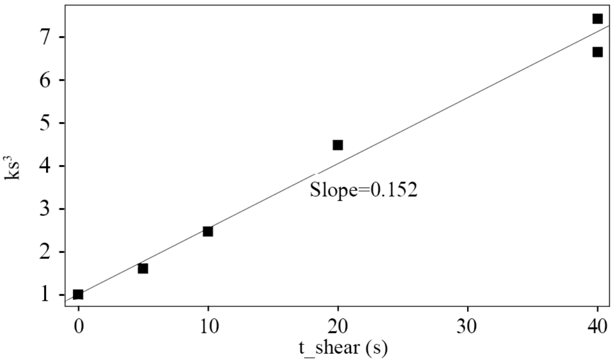

Figure 6. Increase of nucleation density as a function of shearing time.

$$\frac{N_s}{N_{s0}} = 1 + \frac{0.152}{s} t \tag{5}$$

$$\frac{N_s}{N_{s0}} = 1 + \frac{0.152}{s} t \tag{6}$$

The value found for the slope depends obviously on temperature, shear stress and on the particular material grade. However, the result is consistent with literature indications, considering that Kosher and Fulchiron [40] found that the number of nuclei generated after a shear step of 10 s at 1 s^{-1} and 140°C was 40 times the number of nuclei in quiescent conditions (namely a slope of 4 instead of 0.152), whereas Boutaous et al. [41] found that the number of nuclei generated after a shear step of 3560 s at 1 s^{-1} and 138°C was about 140 times the number of nuclei in quiescent conditions (namely a slope of 0.04 instead of 0.152).

CONCLUSION

This study investigated the effect of flow on the crystallization kinetics of polypropylene using a controlled-stress rheometer. The key findings are summarized below:

- Applying a short step shear stress significantly increased the rate of polypropylene crystallization compared to a non-stressed sample. This phenomenon is attributed to stress-induced orientation of macromolecules, which promotes nucleation.
- The increase in viscosity, due to crystallization, occurred faster with longer durations of the applied shear stress. This suggests a higher nucleation density with longer stress exposure.
- By shifting the time axis based on a calculated parameter (k_s), the viscosity data for all tests

collapsed onto a single mastercurve. This confirms the consistency of the model describing the stress-crystallization relationship.

- Nucleation Rate Estimation: The ks parameter, related to the nucleation density at the end of the shear step, increased linearly with stress duration. This allowed for the estimation of the nucleation rate during shear to be 0.152 s^{-1} N_{s0}, being N_{s0} the number of nuclei in quiescent conditions. This value is in the range reported in the literature.

These findings provide valuable insights into the influence of flow fields on polypropylene crystallization behavior. The observed stress-induced enhancement in crystallization kinetics can be crucial for optimizing processing conditions in applications like injection molding and film casting.

CONFLICTS OF INTEREST

The author has no competing interests to declare that are relevant to the content of this article.

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