Crystallinity and Linear Rheological Properties of Polymers

The crystallization of a polymer melt, taking place during transformation processes, has a great impact on the process itself, mainly because it causes a large increase in the viscosity (hardening). Knowledge of the hardening kinetics is important for modeling and controlling the transformation processes. In this work, first an overview is given of the experimental and modeling work on the hardening of crystallizing polymers. Next, we present isothermal crystallization experiments using differential scanning calorimetry (DSC) and rotational rheometry to measure the dynamic viscosity. The evolution of the relative crystallinity and normalized complex viscosity are correlated by a novel technique which allows simultaneous analysis of several runs, even if they are not carried out at same temperatures; the main requirement with the traditional technique. The technique, described in detail in this paper, provides an experimental relationship between the crystallinity and the hardening, i.e. the increase in the viscosity. Moreover, by measuring the dynamic viscosity at different frequencies, surprisingly, a master curve is obtained which combines the effects of shear rate, temperature and the level of crystallinity.

1 Introduction

Most of the polymer production processes (injection molding, fiber spinning, film casting) involves a forming step of the melt, followed by the solidification, mainly due to cooling. For semi-crystalline polymers the solidification implies the creation of ordered structures (so called crystallites), if the process conditions allow for that (e.g. if the cooling rate is not too high). Of course, during the solidification the rheological response of the material changes from a fluid-like behavior towards a solid-like behavior. Detailed knowledge of the material rheology during the solidification is of importance for process control and process modeling.

A number of researchers have investigated the rheology of crystallizing materials. An overview of this work, in terms of the experimental work done and the proposed modeling, is reported in the following section. The experimental data reported in the literature show a large spreading, see Fig. 1. As a consequence, the (empirical) models are of use if, and only if, they are applied to the material on which they were fitted and, thus, they are useless for process simulation codes.

The most critical point in the experimental work on rheology during crystallization is that the evolution of the crystallinity, \( n_g(t) \), and of the hardening evolution, \( \Gamma(t) \), a “Normalized Rheological Function” (NRF), are usually determined during two different experiments, carried out on two different devices. The target function, the hardening behavior \( \Gamma(n_g) \), is obtained by elimination of the time. Due to the stiffness of the two functions this is usually a source of, potentially large, errors. Moreover, the material behavior strongly depends on the temperature. Therefore, if the two experiments were carried out under even small temperature differences, the results can be completely wrong.

The aims of this work are to present a technique able to provide reliable rheological data for crystallizing polymers and to describe these data by a simple model that is easy to implement in a numerical code.

2 State of the Art

2.1 Experimental Results from Literature

The literature related to the effect of crystallinity on rheology is rather limited, mainly because of the experimental difficulties...
in measuring simultaneously crystallinity and rheological functions. Usually separate tests are carried out to measure crystallinity and rheology, taking care that the different samples experience the same thermal histories. For an iPP under isothermal conditions \((T = 135 \text{ and } 140 ^\circ C)\), Titomanlio et al. (1997), measured the crystallinity evolution using DSC and the viscosity evolution using a rotational rheometry in steady motion at very low shear rate \((\gamma = 0.01 \text{ l/s})\). Eliminating the time they got the desired relationship describing the increase in viscosity due to crystallinity. Pantani et al. (2000) performed similar isothermal tests \((T = 140 \text{ and } 143 ^\circ C)\), working with a different iPP and measuring complex viscosity (instead of viscosity) for one frequency, \(\omega = 1 \text{ rad/s}\). Han and Wang (1997) measured the viscosity of a PET during a cooling test (from 290 to 230\(^\circ C\)) using a rotational rheometry in steady motion \((\gamma = 0.1 \text{ l/s})\), and simulated the crystallinity evolution during the test with a kinetic model tuned using DSC, operated under isothermal conditions. Boutahar et al. (1998) investigated the isothermal crystallization behavior of a PE \((T = 126.2 ^\circ C)\) and of an iPP \((T = 135 ^\circ C)\) by DSC, and the rheological behaviors at same temperatures using dynamical oscillatory tests, at various frequencies \((\omega = 0.316 \text{ to 100 rad/s})\).

Pogodina and Winter (1998) measured the rheological behavior of several iPPs using dynamical oscillating tests \((T = 140 ^\circ C)\), and for one of them they estimated also the crystallinity using a model from literature (Kim et al., 1993) that was tuned by DSC, operated isothermally in the temperature range 123.8 to 136.1 \(^\circ C\). Acierno and Grizzuti (2003) proposed a new technique, named “inverse quenching”, in which a given level of crystallinity is obtained keeping the sample at a crystallization temperature \((T = 138 ^\circ C)\) working with an iPP for a specified time and then heating fast the sample to a temperature at which the crystallization kinetic is negligible (the inverse quenching step) and the rheological measurements are easy to perform \((T = 158 ^\circ C)\). They reported both the dynamical modulus, measured for different frequencies, for several crystallization times \((\text{i.e. for samples that were kept at the crystallization temperature for different time intervals, giving rise to different levels of crystallinity})\), and the heat released during the crystallization in a DSC at 138 \(^\circ C\). With the crystallinity obtained from DSC signal, it is straightforward to achieve the relationship between the crystallinity and the complex viscosity. The experimental conditions of the papers discussed are resumed in Table 1, and the data, taken from this literature are summarized in Fig. 1 in terms of the normalized rheological function \((\text{NRF})\) \(\Gamma = \text{viscosity of the crystallizing material/viscosity of the melt measured at the same conditions (temperature, shear rate or oscillatory frequency) versus the degree of space filling } \xi_p\), which is equivalent to the relative crystallinity. Apart from the data of Han and Wang (1997) all the data are for different iPPs. From Fig. 1 it is evident that the viscosity always shows an abrupt increase when crystallization proceeds. However, there is little agreement between the experimental data: if a critical crystallinity is identified as the level at which the viscosity increases one order of magnitude, the critical crystallinity ranges from 2 to 10 % following (Titomanlio et al., 1997; Pantani et al., 2001; Pogodina and Winter, 1998). The critical crystallinity is more than 10 % following Han and Wang (1997) and even more than 40 % in the work of Boutahar et al. (1998).

Furthermore, looking at the results summarized in Fig. 1, the effect of temperature is hard to address: most of the researchers did not investigate more than one temperature. Pantani et al. (2001) found results practically independent from temperature. Titomanlio et al. (1997) found that for a given amount of crystallinity the normalized viscosity is larger at lower temperature. The effect of oscillatory frequency has also been analyzed: a higher frequency shifts the ‘hardening’ curve towards higher crystallinity (Pogodina and Winter, 1998; Acierno and Grizzuti, 2003); and, less evident, in the results of (Boutahar et al. 1998).

Recently Pogodina et al. (2001), carefully analyzed the isothermal crystallization of an iPP at 148 \(^\circ C\). They observed spherulitical growth using optical microscopy, the SALS invariant evolution and the moduli using a rheometer. They also attempted to perform DSC measurements, but the crystallization rate at this temperature is too low to produce any detectable enthalpy peak. The ‘gel-point’ (roughly defined as the time for which the storage modulus reaches a value equal to 10 % of its final value) was observed after about 25 000 s, just before spherulites impinge, at a degree of space filling, \(\xi_p\), between 0.20 and 0.28 (they report an absolute crystallinity \(\xi = 0.6 \cdot \xi_p = 0.12 \text{ to } 0.17\)). Thus, the critical crystallinity they observed is intermediate between the ones reported above and summarized in Fig. 1.

Others have carried out rheological measurements on crystallizing samples, for example (Vleeshouwers and Meijer, 1996; Wassener and Maier, 2001; Floudas et al., 2000), but there are no reliable crystallinity results in these papers, i.e. a rheology/crystallinity analysis is not possible.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Crystallinity measurement</th>
<th>Measured rheological property</th>
<th>“Hardening” function (NRF)</th>
<th>Material</th>
<th>Temperature(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titomanlio et al., 1997</td>
<td>DSC</td>
<td>viscosity</td>
<td>(\Gamma = \eta/\eta_0)</td>
<td>iPP</td>
<td>135 (^\circ C), 140 (^\circ C)</td>
</tr>
<tr>
<td>Pantani et al., 2001</td>
<td>DSC</td>
<td>complex viscosity</td>
<td>(\Gamma = \eta/\eta_0)</td>
<td>iPP</td>
<td>140 (^\circ C), 143 (^\circ C)</td>
</tr>
<tr>
<td>Bouthahar et al., 1998</td>
<td>DSC</td>
<td>complex viscosity</td>
<td>(\Gamma = \eta/\eta_0)</td>
<td>iPP</td>
<td>135 (^\circ C)</td>
</tr>
<tr>
<td>Pogodina and Winter, 1998</td>
<td>Model from literature (Kim et al., 1993)</td>
<td>complex viscosity</td>
<td>(\Gamma = \eta/\eta_0)</td>
<td>iPP</td>
<td>150 (^\circ C)</td>
</tr>
<tr>
<td>Acierno and Grizzuti, 2003</td>
<td>DSC</td>
<td>complex viscosity</td>
<td>(\Gamma = \eta/\eta_0)</td>
<td>iPP</td>
<td>measurement made at 158 (^\circ C) and shifted at 138 (^\circ C)</td>
</tr>
<tr>
<td>Han and Wang, 1997</td>
<td>Model tuned by DSC meas.</td>
<td>viscosity</td>
<td>(\Gamma = \eta/\eta_0)</td>
<td>PET</td>
<td>measurement made during a cooling test</td>
</tr>
</tbody>
</table>

* iPP 0 iPP 135 \(^\circ C\), 143 \(^\circ C\) * iPP 150 \(^\circ C\) * measurement made at 138 \(^\circ C\)
2.2 Models Based on Rheology of Suspensions

The description of the rheological behavior of crystallizing polymers is a fundamental issue and of importance for processes simulation. Two main approaches have been followed to model the effect of the crystallinity on the viscosity:

i) apply models that are developed to describe the behavior of suspensions,

ii) apply empirical formulas that capture the steep increase in viscosity.

Empirical models are only useful after fitting reliable experimental data.

A summary of the models developed in the field of the rheology of suspension is reported in Table 2 and predictions of the models are reported in Fig. 2. Detailed reviews on the rheology of suspensions (experiments/modeling) can be found in Metzner (1985) and Khan and Prud’Homme (1987).

From Fig. 2 it is evident that the models, except two, predict similar behavior, i.e. the critical filler content (the filler content that causes an order-of-magnitude increase of viscosity with respect to the solvent value, \( \Gamma = 10 \)) ranges between 35 to 50 %. The two exceptions are the Einstein and the Batchelor expressions, which were developed to describe dilute suspensions behavior and, therefore, are limited only up to 5 to 10 % of filler content. The Frankel and Acrivos equation is not suitable to describe the dilute suspensions behavior (low values of filler content predicts \( \Gamma < 1 \), i.e. suspension viscosity lower than solvent viscosity).

<table>
<thead>
<tr>
<th>Model</th>
<th>Reference</th>
<th>Note(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma = 1 + \frac{5}{2} \xi_g )</td>
<td>Einstein, 1906 and 1911</td>
<td>Diluted suspension of rigid, non interacting, spheres in a Newtonian solvent</td>
</tr>
<tr>
<td>( \Gamma = 1 + \frac{5}{2} \xi_g + 6.2 \xi_g^2 )</td>
<td>Batchelor, 1977</td>
<td>Diluted suspension of rigid interacting spheres in a Newtonian solvent</td>
</tr>
<tr>
<td>( \Gamma = \left( \frac{1 - \xi_g}{\xi_{g_{\text{max}}}} \right)^{-c_{\text{max}}} )</td>
<td>Ball and Richmond, 1980</td>
<td>Concentrated suspension of rigid spheres, ( \xi_{g_{\text{max}}} ) being the maximum volume fraction occupied by the spheres</td>
</tr>
<tr>
<td>( \Gamma = \exp \left[ \frac{5}{2} \frac{\xi_g}{1 - (\xi_g/\xi_{g_{\text{max}}})} \right] )</td>
<td>Mooney, 1951</td>
<td>Concentrated suspension of rigid interacting spheres, ( \xi_{g_{\text{max}}} ) being the maximum volume fraction occupied by the spheres</td>
</tr>
<tr>
<td>( \Gamma = 1 + \frac{5}{2} \xi_g + \frac{9}{4} \left( \psi(1 + 0.5\psi)(1 + \psi) \right) )</td>
<td>Graham, 1981</td>
<td>Concentrated suspension of rigid interacting spheres, ( \xi_{g_{\text{max}}} ) being the maximum volume fraction occupied by the spheres</td>
</tr>
<tr>
<td>( \psi = 2(1 - \sqrt{\xi_g/\xi_{g_{\text{max}}}})/(\sqrt{\xi_g/\xi_{g_{\text{max}}}}) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Gamma = \frac{9}{8} \left( \frac{\xi_g}{\xi_{g_{\text{max}}}} \right)^{1/3} )</td>
<td>Frankel and Acrivos, 1967</td>
<td>Concentrated suspension of rigid interacting spheres, ( \xi_{g_{\text{max}}} ) being the maximum volume fraction occupied by the spheres</td>
</tr>
<tr>
<td>( \Gamma = \left( 1 - \xi_g/\xi_{g_{\text{max}}} \right)^{-c_{\text{max}}[\eta]} )</td>
<td>Krieger and Dougherty, 1959</td>
<td>Concentrated suspension of particles of any shape, ( \xi_{g_{\text{max}}} ) being the maximum volume fraction occupied by the spheres and ( [\eta] ) being the intrinsic viscosity of the solvent</td>
</tr>
<tr>
<td>( \Gamma = \left( 1 - \xi_g/\xi_{g_{\text{max}}} \right)^{-2} )</td>
<td>Kitano et al., 1978 and 1981</td>
<td>Concentrated suspension of particles of any shape, ( A ) being a shape coefficient (( A = 0.68 ) for smooth spheres)</td>
</tr>
</tbody>
</table>

Table 2. Models based on rheology of suspensions (\( \Gamma \) = normalized rheological function = suspension viscosity/solvent viscosity; \( \xi_g \) = filler content)

2.3 Empirical Models

Some of the empirical models adopted for the description of the viscosity of crystallizing polymers, are summarized in Table 3, and their behavior is shown in Fig. 3 where the parameters values reported in original papers where used. The parameter \( \Gamma(\infty) \) in Khanna (1993) and in Boutahar et al. (1998) (for Colloid-Like
Keeping in mind the experimental data of Fig. 1, the linear trend ($\Gamma$ vs $\xi_g$) predicted by Khanna (1993) and Katayama & Yoon (1985) should be excluded, because it doesn’t fit any of the observed real behavior. All the other models could, in principle, properly describe the crystallinity/viscosity relation by adopting the parameter values. For example, the expression adopted by Zuidema et al. (2001), using their parameter values, predicts an unrealistic value (too low) of the hardening for a fully crystallized polymer ($\Gamma$ (Zuidema et al.) is of the order of tens). Doufas et al. (2000), used the same formula, but with their choice of parameters, for $\xi_g = 1$, $\Gamma$ (Doufas et al.) is very large, of the order of $10^{25}$.

### 3 Experimental

#### 3.1 Materials

Two commercial iPP homopolymers have been used in the frame of this work: Montell T30G ($M_w = 376 000$, $M_n = 56 000$, tacticity = 87.6 % mmmm), and DSM 15M10 ($M_w = 350 000$, $M_n = 62 500$, tacticity = 96.2 % mmmm).

![Fig. 3. Normalized rheological $\Gamma$ versus degree of space filling $\xi_g$, as predicted by the empirical models listed in Table 2. For each model, the parameter values have been taken from original papers](image)

<table>
<thead>
<tr>
<th>Model</th>
<th>Reference</th>
<th>Parameter values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma = \exp\left(a_1\xi_g + a_2\xi_g^2\right)$</td>
<td>Doufas et al., 2000</td>
<td>$a_1$</td>
</tr>
<tr>
<td></td>
<td>Zuidema et al., 2001</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Shimizu, 1985</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Yarin, 1992</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Han and Wang, 1997</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Heiber, 2002</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma = 1 + a_1\xi_g^{a_2}$</td>
<td>Katayama, 1985</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>Khanna, 1993</td>
<td>$\Gamma(\infty) = 1$</td>
</tr>
<tr>
<td>(Colloid-like systems)</td>
<td>Boutahar et al., 1998</td>
<td>$\Gamma(\infty)$</td>
</tr>
<tr>
<td></td>
<td>Zlubicki, 1988</td>
<td>$\neq 0$</td>
</tr>
<tr>
<td>(Suspension-like systems)</td>
<td>Boutahar et al., 1998</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Titomanlio et al., 1997; also adopted by Guo and Narh, 2001</td>
<td>$a_1$, $a_2$, $a_3$ = fitting parameters</td>
</tr>
<tr>
<td></td>
<td>Tanner, 2003</td>
<td>$a_1$, $a_2$ = fitting parameters</td>
</tr>
</tbody>
</table>

Table 3. Empirical models ($\Gamma = \text{normalized rheological function} = \text{viscosity of crystallizing polymer} / \text{viscosity of the melt}; \xi_g = \text{degree of space filling, i.e. relative viscosity}$)
3.2 Methods

Calorimetric tests have been performed (Mettler-Toledo DSC822) using aluminum pans of 40 µl in volume, liquid nitrogen as freezing fluid, working under inert gas flux (nitrogen, 100 ml/min). The experiments consisted of melting a sample at high temperature (240 °C) for a time sufficient to delete the memory of previous crystallization (30 min), a cooling step carried out at the maximum cooling rate allowed by the instrument (60 °C/min) and isothermal crystallization step at the test temperature.

Rheological tests have been performed on two different rotational rheometers (strain controlled: Rheometrics RDS II (Swartjes, 2001), stress controlled: Rheometrics SR5000) using a plate-cone configuration, 25 mm diameter, cone angle 0.1004 rad. The experiments were carried out at the frequency of $\omega = 1$ rad/s, keeping the stress constant at 1000 Pa for the iPP T30G, and at various frequencies ($\omega = 2.5$, 5, 10 and 20 rad/s), keeping the strain constant at 0.4 % for the iPP DSM 15M10. The thermal histories were programmed as close as possible to the thermal histories experienced by the sample in the DSC: the cooling step from the annealing temperature to the test temperature was obtained in two steps, the second one being carried out at lower cooling rate (30 °C/min), to minimize the temperature undershoot that normally occurs. Still an under-cooling of 1.5 ± 2.5 °C was observed during the tests, before the test temperature has been reached and kept constant. The zero time, $t_0$, was defined as the time at which the temperature passes for the first time the test temperature value.

4 Data Analysis

4.1 Experimental Data

Isothermal DSC tests have been performed at different temperatures; $T_{15M10} = \{122, 126, 128, 130, 132, 134\} °C$ for the iPP T30G and $T_{15M10} = \{128, 130, 132, 134, 136, 138\} °C$ for the iPP 15M10. By subtracting the baseline, integration and normalization the time-evolutions of relative crystallinity (or degree of space filling) is obtained, see Fig. 4.

There are no important differences in molecular weight and in molecular weight distributions of the two polymers. The iPP 15M10 crystallizes at higher temperature than the iPP T30G, most probably due to its higher tacticity (96.2 % for iPP 15M10 versus 87.6 % for iPP T30G), that promotes the nuclei formation and/or the growth rate.

Different isothermal rheological experiments ($M_{T30G} = 6$ and $M_{15M10} = 5$) have been performed at temperatures $T_{T30G} = \{128, 130, 132, 134, 136, 138\} °C$ and $T_{15M10} = \{134, 136, 138, 140, 142\} °C$. The ratio between the complex viscosity $\eta^*$ and its initial value, the melt complex viscosity $\eta_0$, has been adopted as the “normalized rheological function”, NRF, $\Gamma = \eta^*/\eta_0$, which is used as a measure for the melt hardening. Results are given in Fig. 5. For the DSM15M10 only data for $\omega = 10$ rad/s is shown and for the T30G only for $\omega = 1$ rad/s.

Notice that the temperatures for the two different measurements (calorimetric and rheological) are not the same, since the intrinsic characteristics of the instruments limit the accessible temperature ranges in a different manner (e.g., with reference to iPP T30G, a temperature higher than 134 °C in the DSC causes an enthalpy release too slow to be detected, a temperature lower than 128 °C in the rheometer causes a crystallization so fast that the initial plateau is not detectable).

The normalized function $\Gamma = \Gamma(\xi_g)$ is usually determined from the values of crystallinity and viscosity measured after the same residence time at the test temperature during two tests carried out with the same temperature history. A more general method for data analysis, explained in the next section, allows to elaborate data obtained at different temperatures (not too far from each other in different experiments), like the series used in this work, $T_g$ and $T_r$.

4.2 General Analysis Technique

The procedure adopted to analyze the data is described in the following steps:

1. The time required to obtain a selected value of degree of space filling (relative crystallinity), $\xi_g$, is obtained from Fig. 4 as function of temperature;
2. The data sets $\{T_g^j, \log(\xi_g^j)\}$ are shown in Fig. 6 (filled squares). They are described by:
   \[
   \log (t) = a(\xi_g) + b(\xi_g) T. \tag{1}
   \]
   The intercept, $a$, and the slope, $b$, of this line are functions of the relative crystallinity $\xi_g$ only (Fig. 6, dashed line);
3. The rheological data are analyzed in the same way, i.e. the time values required to reach a given value of $\Gamma$ for the different temperatures, are obtained from Fig. 5.
5. These two relations could a priori be independent; i.e. the linear relationship between crystallinity and hardening, for a given value of crystallinity, being independent on the way in which this amount of crystallinity was produced. The same amount of crystallinity, given by either a large number of small spherulites (low temperature) or by a small number of large spherulites (high temperature), seems to give the same rheological hardening of the material.

4. Drawing \( \{T_1 \}, \log(t_1) \) in Fig. 6 shows that these data also follow the same linear trend as \( \{T_1 \}, \log(t_1) \) and this is observed for all \( \Gamma \)'s. Thus, it is experimentally observed that in the log(t) vs. T plane both the kinetic and the rheological data are described by a straight line with the same slope. To our knowledge it is the first time that the dependence upon temperature of the logarithm of the crystallization time is locally linear with the temperature (i.e., within a not too large range of temperatures). It has to be emphasized that it includes both the evolution of crystallinity and the effect of crystallization on viscosity.

5. These two relations could a priori be independent; i.e. the temperature dependence of the crystallization kinetics could be different from the temperature dependence of the rheological hardening kinetics. Otherwise, if a relationship exists between crystallinity and hardening, for a given value of crystallinity \( \xi_g \), the corresponding value for \( \Gamma \) minimizes the function \( E(\Gamma) \):

\[
E(\Gamma) = \sum_{i=1}^{M} \left\{ \log \left[ T_1^{(i)} \right] - \left[ \alpha \left( \xi_g \right) + \beta \left( \xi_g \right) \Gamma^{(i)} \right] \right\}^2.
\] (2)

For a given value of \( \xi_g \), the function \( E(\Gamma) \) shows a minimum for a single value of \( \Gamma \) which is thus associated to the given crystallinity value. For that value of \( \Gamma \) it occurs that the sets \( \{T_1, \log(t_1)\} \) describe the same line as given by Eq. 1 or, in other words, they match the calorimetric data. Thus: in the temperature range considered, a unique relationship between crystallinity \( \xi_g \) and hardening \( \Gamma \) exists.

This is another result and somehow surprising. It means that, at least in the temperature range investigated, the hardening behavior in terms of LVE is only related to the total amount of crystallinity, being independent on the way in which this amount of crystallinity was produced. The same amount of crystallinity, given by either a large number of small spherulites (low temperature) or by a small number of large spherulites (high temperature), seems to give the same rheological hardening of the material.

Fig. 6 shows an example of applying the method described. The rheological data \( \{T_1, \log(t_1)\} \) are reported as open symbols. Re-applying the method for different values of crystallinity \( \xi_g \), an ensemble of couples \( \{\xi_g, \Gamma\} \) is obtained that constitutes the relationship \( \Gamma = \Gamma(\xi_g) \), applicable in the temperature range investigated (T = 122 to 138 °C) and to the frequency adopted in the rheological tests (\( \omega = 1 \) rad/s) for iPP T30G. A similar analysis was carried out for iPP 15M10 (for all the frequencies investigated, \( \omega = 2.5, 5, 10 \) and 20 rad/s), and the results are valid in the temperature range investigated (T = 128 to 144 °C).

5 Results and Discussions

In Fig. 7 the sets \( \{\xi_g, \Gamma\} \) (degree of space filling and normalized rheological function) are reported for both iPP T30G (at \( \omega = 1 \) rad/s) and iPP 15M10 (\( \omega = 2.5, 5, 10 \) and 20 rad/s).

In the following a formal description of the viscosity as a function of angular frequency (shear rate), temperature and degree of space filling is given. We start with a model for the complex viscosity.

The complex viscosity as a function of the angular frequency can be described with Carreau-Yasuda model (Hieber and Chiang, 1992):

\[
\eta^* = \eta_\infty \left[ 1 + \left( \frac{\omega \lambda}{\alpha} \right)^2 \right].
\] (3)

For the the iPP 15M10 the parameter values are (Zuidema et al., 2001) \( \eta_\infty = 0, \eta_0 = 3877 \text{ Pa} \cdot \text{s}, \lambda = 0.0657 \text{ s}, \alpha = 0.4824 \)
and $n = 0.2192$. The temperature dependency of the viscosity is described by an Arrhenius expression (Zuidema et al., 2001):

$$a_1(T) = \exp \left[ \frac{E_{\text{ref}}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right],$$

(4)

with $E_{\text{ref}} = 46.04 \text{ kJ/mol}$ and $T_{\text{ref}} = 493.15 \text{ K}$. The viscosity, at temperature $T$ is obtained from the viscosity $\eta_{\text{ref}}$ at $T_{\text{ref}}$ by:

$$\eta^*(T, \omega) = \eta_{\text{ref}}(\omega \cdot a_1) \cdot a_1,$$

(5)

Following the same approach, the effect of crystallinity on rheology can be accounted for adding the hardening function, $a_2$, as an additional shift factor acting on $\omega$ and $\eta_{\text{ref}}$ which here is the viscosity curve at $T_{\text{ref}}$ and $a_2 = 0$:

$$\eta^*(T, \omega, \xi_g) = \eta_{\text{ref}}(\omega \cdot a_1 \cdot a_2) \cdot a_1 \cdot a_2,$$

(6)

The hardening data can be fitted by a suitable relationship, only meant to give an “as good as possible” description of the data:

$$a_2(\xi_g) = 10^6 \xi_g^b.$$

(7)

Other expressions are of course possible and it is desirable to replace expression (Eq. 7) by a more physically based expression in future work. However, this is not of importance here as it is our aim to demonstrate the experimental method and results.

For iPP 15M10 the hardening parameters are: $\{a = 3.875, b = 1.236\}$. With these parameters, and using Eqs. 6 and 7, the viscosity at $132^\circ \text{C}$ (which is an average temperature for the rheological tests) agrees quite well with experimental data, see Fig. 8.

Following the same reasoning but adopting a Cross-Arrhenius model to describe the melt rheology, also the data for iPP T30G, only available for a single frequency, have been reproduced. The values of parameters determined to fit the hardening behavior of iPP T30G are: $\{a = 12.073, b = 3.166\}$. Results of fitting Eqs. 6, 7 are shown in Fig. 7 (solid line).

Thus, the full model (Eqs. 6, 7) allows calculation of viscosity as function of temperature, oscillation frequency and crystallinity.

The approach is equivalent to adopt a time-hardening superposition, (similarly to the time-temperature superposition): the viscosity observed at a frequency $\omega$ and in the absence of crystallinity ($\xi_g = 0$) is the same viscosity observed at a frequency $\omega \cdot a_1(\xi_g)$. This means that it is possible to create a “master curve” for the effect of crystallinity on viscosity. In Fig. 9 the viscosity versus frequency curve is drawn using Eqs. 6, 7 (at $T = 132^\circ \text{C}$) and the data already reported in Fig. 8 (which are only a fraction of the data reported in Fig. 7) are added following the shift procedure. Indeed, a master curve is obtained.

The data for iPP T30G were obtained working at a single frequency ($\omega = 1 \text{ rad/s}$), and the hardening function has been tuned on the basis of these data. Assuming the time-hardening superposition principle to apply also for this polymer, the availability of these data allows to predict the viscosity of the material at any crystallinity and at any frequency.

With the goal of building a model applicable in process simulation, the results obtained in term of complex viscosity vs. frequency should be extended to a relation between viscosity and shear rate.

The Cox-Merz rule could be applied for this, however, this rule is known to be not fully reliable for crystallizing materials.
(more specific; for two-phase materials in general). However, as a first approximation, this is the most straightforward way to introduce the effect of crystallinity on rheology, and it represents a remarkable improvement with respect to the way commonly adopted in simulation codes (for example the concept of “solidification temperature”, in which the viscosity is taken to be very large as soon as the material temperature reaches values under a given limit).

6 Conclusions

Isothermal crystallinity measurements using DSC and isothermal rheological measurements have been performed. A data analysis method has been proposed and applied, the method compares simultaneously all the experiments performed in a temperature range and that allows to relate the hardening function which holds, at least in the temperature range investigated.

The new method of analysis overcomes the requirement to carry out calorimetric and rheological tests exactly at same temperature. The method has been applied to two iPP grades for which a relationship between crystallinity and viscosity hardening has been obtained. The viscosity hardening functions, \(a_c(\gamma_0)\), was adopted also to describe into a master curve the combined effects of shear rate and crystallinity on the viscosity by shifts both on the shear rate and on the viscosity axes, similarly to the procedure identified as the well-known time-temperature superposition principle.

References


Date received: November 6, 2006
Date accepted: March 16, 2007

You will find the article and additional material by entering the document number IPP2006 on our website at www.polymer-process.com