

Pressure Effect on Viscosity for Atactic and Syndiotactic Polystyrene

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Summary

The effect of pressure on viscosity is an important but often overlooked aspect of the flow properties of polymeric materials. Generally, an exponential dependence (the so-called Barus equation: $\eta = \eta_0 \exp(\beta P)$) can be adopted to describe this effect. In this work two polymers (an atactic and a syndiotactic Polystyrene) were characterized as far as the effect of pressure on viscosity is concerned by analyzing the non-linearities in the so-called Bagley plots. The results obtained show that for both materials the average value of β is in the range $1\text{--}3 \cdot 10^{-8} \text{Pa}^{-1}$. No relevant effects of temperature and shear rate were detected in the range analyzed. The data obtained were also described by means of a Cross-Vogel model, which reproduces the main features of experimental data.

Introduction

Typical pressure levels encountered during polymer processing operations, especially in injection molding, can be very high (of the order of several tens of MPa). Under these conditions, the common assumption that polymer viscosity is constant with pressure can be misleading. Despite the considerable efforts spent in an accurate modeling of polymer processing, a huge underestimation of pressure drops in runners and dies can result from neglecting the increase of viscosity induced by pressure in the material database. On its turn, this underestimation can result in incomplete filling of cavities, burnings and longer processing times.

In the last decade, studies have been focused by several research groups [1–4] to set-up experimental methods to evaluate the effect of pressure on the rheological behavior of polymers (a review of these methods is reported for instance by Goubert et al. [2]). The most sophisticated techniques consist in high-pressure versions of standard pressure rheometers. These newly developed devices incorporate a valve or a second piston at the die exit to control the flow and increase the average pressure under which the melt flows. Another possibility is to use slit rheometers, and recording the pressure profile along the die length [5]. The effect of pressure on viscosity is in this case estimated by the analysis of a non-linear pressure profile. Despite the accessibility of these relatively new techniques, the most used method is up to now represented by the analysis of non-linearities in the so-called Bagley plots, obtained by standard capillary

rheometers [6]. Its simplicity allows a rapid estimation of the phenomenon by standard capillary measurements, accessible to anyone. This technique, however, suffers from a scarce sensitivity and provides quite reliable results only with materials which present a large effect of pressure on viscosity. In this work, this technique is adopted to characterize two polystyrene melts, namely an atactic (aPS) and a syndiotactic one (sPS) in a range of conditions of interest for polymer processing. Experimental results were discussed in terms of accuracy and sensitivity of the analysis adopted.

Analysis of non-linearities in Bagley plots

When using capillary data, it is necessary to take into account the extra pressure drop occurring at the entrance of the die. This is normally done by plotting the pressure drop over the capillary as a function of its aspect ratio (length-to-diameter: L/D) for a given shear rate (the Bagley plot [7]). If the viscosity does not depend on pressure, and the flow is isothermal, this plot is linear, and the extrapolation to zero L/D yields the entrance pressure drop. Nonlinear Bagley plots are however often found for thermoplastic polymers, and are commonly attributed to the effect of pressure on viscosity [5, 8]. In this case, a different analysis is required to characterize material viscosity.

Classical analysis

The momentum balance over the capillary can be written as

$$\sigma_{ow} e^{\beta P} \frac{4}{D} = \frac{dP}{dz} \quad (1)$$

where z is the flow direction, P is the pressure, L/D is the capillary aspect ratio, σ_{ow} is the stress at capillary wall at zero pressure and the Barus equation [9]

$$\eta = \eta_0 e^{\beta P} \quad (2)$$

is adopted to describe the effect of pressure on viscosity, through the parameter β , whose dependence on pressure is assumed to be negligible.

Integrating eq. (1) over the capillary length, one obtains

$$\sigma_{ow} 4 \frac{L}{D} = \frac{e^{-\beta P_L} - e^{-\beta P_0}}{\beta} \quad (3)$$

where P_0 and P_L are the pressures at capillary entrance and exit, respectively. If exit pressure drops can be neglected, eq. (3) can be written as

$$e^{-\beta P_0} = 1 - \beta \sigma_{ow} 4 \frac{L}{D} \quad (4)$$

The pressure at capillary entrance, P_0 , is given by the difference between P_p , namely the pressure imposed by the plunger, and P_B , which is the entrance pressure drop. Equation (4) can thus be written as

$$P_p = P_B - \frac{1}{\beta} \ln \left(1 - \beta \sigma_{ow} 4 \frac{L}{D} \right) \quad (5)$$

This equation is highly non-linear, and the attempts of obtaining the parameters P_B , β and σ_{ow} by a non-linear fitting on the basis of capillary data are quite problematic for small values of β (which is typically of the order of 10^{-9} - 10^{-8} Pa $^{-1}$ [3]). In this cases the equation becomes nearly insensitive to variations of β . This means that, if a non-linear fitting is attempted, the procedure converges to a value of β very close to the starting one. This is the reason why several approaches are found in the literature to simplify eq. (5) [2, 10, 11].

The classical approach to the problem [6] provides for a series expansion of the logarithm in eq. (5), which thus becomes, neglecting the higher order terms,

$$P_p = P_B + \frac{1}{\beta} \left[\beta \sigma_{ow} 4 \frac{L}{D} + \frac{1}{2} \left(\beta \sigma_{ow} 4 \frac{L}{D} \right)^2 \right] \quad (6)$$

and eventually the experimentally determined pressure P_p is expressed as a function of the capillary aspect ratio in a quadratic form

$$P_p = a \left(\frac{L}{D} \right)^2 + b \left(\frac{L}{D} \right) + c \quad (7)$$

where

$$\begin{cases} \sigma_{ow} = b/4 \\ P_B = c \\ \beta = 2a/b^2 \end{cases} \quad (8)$$

All the relevant parameters are thus easily determined by a quadratic fitting of data. It should be mentioned that, being the residual of the series expansion positive, higher values of β will be needed to describe the experimental data. The values of β found by the classical analysis of non-linearities in Bagley plots leads thus to an overestimation of β [2].

Alternative approach

In this work a different approach is adopted with respect to the classical one. Rather than the logarithm in eq. (5), the exponential in eq. (4) is approximated up to the second order term, and thus eq. (4) is rewritten as

$$P_0 - \frac{\beta P_0^2}{2} = \sigma_{ow} 4 \frac{L}{D} \quad (9)$$

This series expansion provides a better approximation with respect to the classical analysis if the product βP_0 is less than 0.5 (the remainder being always less than 6%). Due to the low values of β , this condition is verified in most of cases during tests with capillary rheometers.

The pressure at capillary entry, P_0 , can be now substituted by the pressure imposed by the plunger, P_p , if the actual capillary is replaced by a fictive one, having a greater aspect ratio. Equation (9) can be thus rewritten as

$$\frac{L}{D} = -\frac{1}{4\sigma_{ow}} \frac{\beta}{2} P_p^2 + \frac{1}{4\sigma_{ow}} P_p - \frac{e}{D} \quad (10)$$

where e is the additional length which keeps into account the entrance effect on pressure drop.

According to this approach, the capillary aspect ratio is expressed as a function of the experimentally determined pressure P_p in a quadratic form

$$\frac{L}{D} = -a' P_p^2 + b' P_p - c' \quad (11)$$

where

$$\begin{cases} \sigma_{ow} = 1/4b' \\ \frac{e}{D} = c' \\ \beta = \frac{2a'}{b'} \end{cases} \quad (12)$$

The analysis described above requires the data to be plotted in a slightly different way with respect to the classical analysis, namely the axis are switched. It is worth mentioning that, being the residual of the series expansion positive, lower values of β will be needed to describe the experimental data. Differently from the classical analysis, the values of β found by the alternative approach will naturally be underestimated.

Experimental results

Materials

Two materials were adopted in this work: an atactic and a syndiotactic polystyrene. The aPS is a general purpose polystyrene (STYRON 678E by Dow Chemicals, $M_w=250'000$, $M_w/M_n=2.9$), well characterized in the literature (see for instance [12]). Among the most commonly adopted polymers in polymer processing industry, aPS meets with the highest effect of pressure on viscosity [3]. The sPS is a neat resin (QUESTRA QA 101 kindly supplied by Dow Chemicals, $M_w=320'000$, $M_w/M_n=3.9$, syndiotacticity 98%). sPS is a relatively recently developed material, and its behavior in process conditions is not well characterized yet.

Rheometric tests

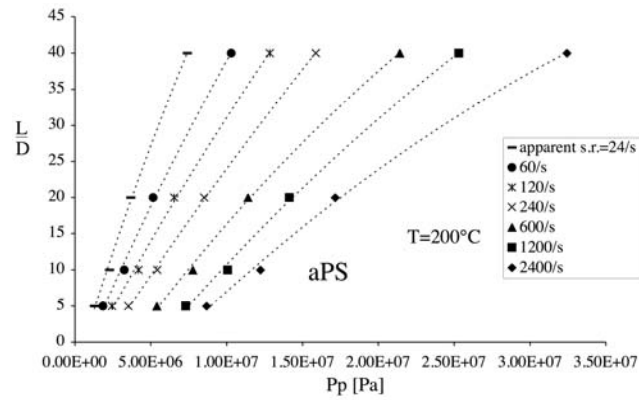
A number of tests with a standard capillary rheometer (CEAST Rheoscope 1000, accuracy $1\text{ daN}\pm 0.5\%$) were conducted. The barrel had a diameter of 9.5mm. A series of capillaries having a diameter of 1mm and with L/D ratios of 5, 10, 20 and 40 was adopted. Apparent shear rates were ranging from 24 s^{-1} to 2400 s^{-1} . The aPS was tested at three temperatures: 200°C , 220°C and 240°C . Only two temperatures were chosen for sPS, namely 280°C and 300°C , due to the extremely narrow process window of this material, which quickly degrades at temperatures higher than 310°C and rapidly crystallizes at temperatures lower than 270°C [13].

The data obtained by standard capillary tests are reported in Figure 1 for aPS and in Figure 2 for sPS. According to the procedure of analysis described above, the pressure imposed by the plunger is reported on the x axis, whereas the capillary aspect ratio is reported on the y-axis.

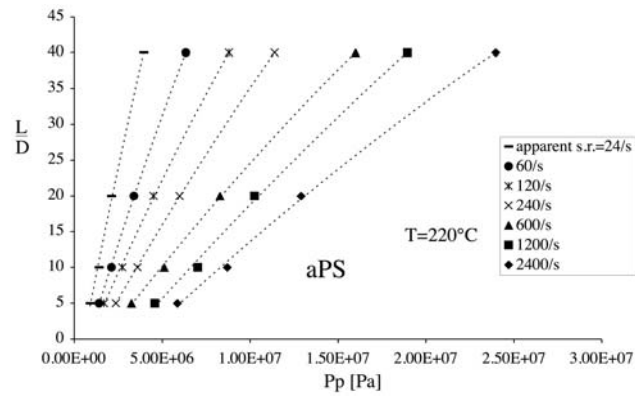
It can be easily noticed that the data deviate from linearity for both materials. This evident features encourages to analyze the data by means of the method delineated above which, as mentioned in the introduction, can be successfully employed especially when the values of β are large.

Analysis of results

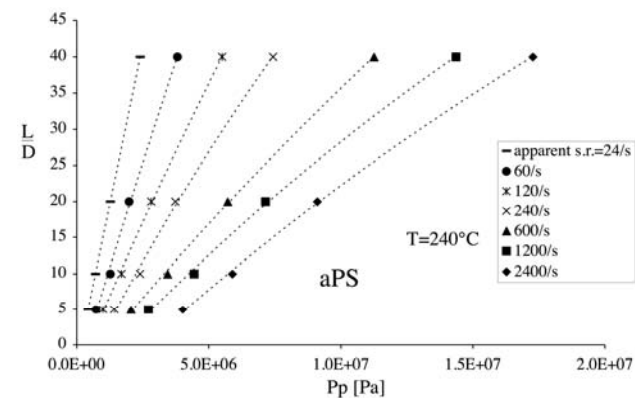
By a best fitting analysis based on eq. (11) the values of wall shear stress at zero pressure and at each apparent shear rate can be obtained. The Mooney-Rabinowitsch correction can thus be applied to the experimental data in order to identify the wall shear rate. In the following, all results will be reported versus the corresponding "true" shear rates. The analysis of uncertainties is rarely reported in the literature when the estimation of the parameter β is derived from non linearities in pressure profiles.



a



b



c

Figure 1. Data obtained on the aPS by standard capillary rheometry. a) 200°C , b) 220°C , c) 240°C . The pressure imposed by the plunger is reported on the x-axis in agreement to the form of equation (10).

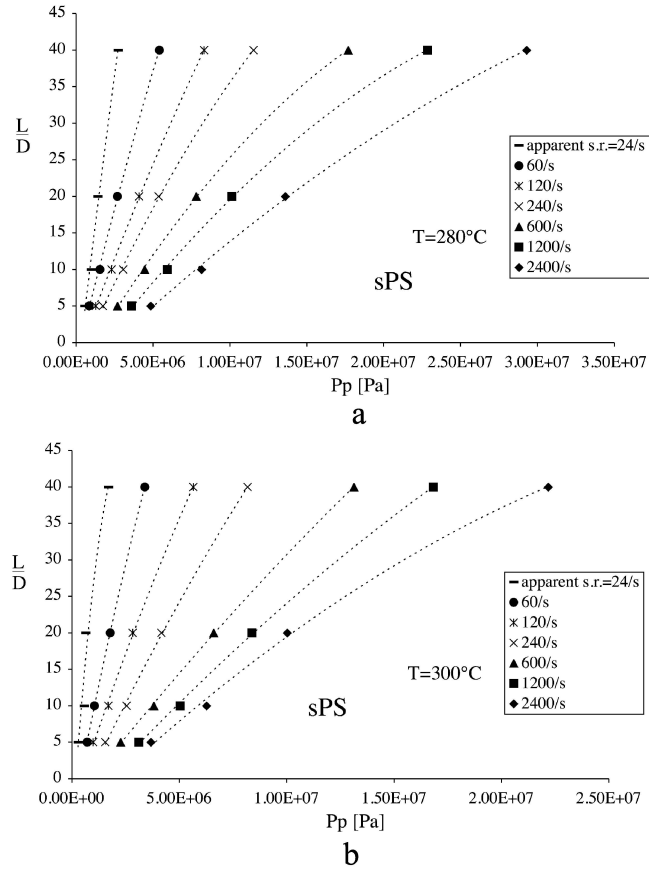


Figure 2. Data obtained on the sPS by standard capillary rheometry. a) 280°C, b) 300°C. The pressure imposed by the plunger is reported on the x-axis in agreement to the form of eq. (10).

In this work, the uncertainties in the coefficients of the best-fit analysis were calculated by means of the general relationship for error propagation:

$$u_f = \sqrt{\sum_{i=1}^N u_{x_i}^2 \left(\frac{\partial f}{\partial x_i} \right)^2} \quad (13)$$

where u_f is the uncertainty in the function f (the one we are interested in) and u_x is the uncertainty in the experimental data (namely in the measured pressure). The same relationship was used to calculate the uncertainties in the values of σ_{0w} (which were found to be less than 15%) and, above all, in the values of β .

The results obtained by the regression of data reported in Figures 1 and 2 according to eq. (11) are reported in Figures 3 and 4 for aPS and sPS, respectively, together with the corresponding uncertainties. Despite of the extreme care in conducting the experiments, which were repeated four times (both in increasing and decreasing shear rates), the uncertainties at the lowest shear rates and at the highest temperatures are quite large for both materials. This happens especially because the pressure levels reached in those conditions are low with respect to the sensitivity of the instrument. Thus, only the data at the highest applied shear rates are reported in Figures 3 and 4.

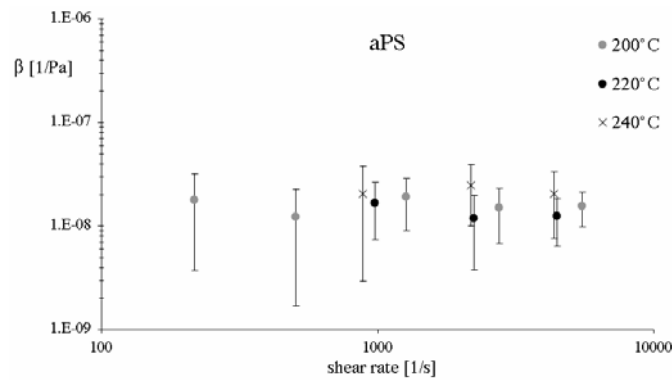


Figure 3. Values of the parameter β for aPS obtained analyzing the data of Figure 1 by means of eq. (11).

As a general comment on the results obtained, it can be noticed that for both materials the average value of β is in the range $1\text{-}3 \cdot 10^{-8}\text{Pa}^{-1}$. Data indicate that the effect of pressure on sPS is slightly larger than for aPS (2.1 vs. $1.4 \cdot 10^{-8}\text{Pa}^{-1}$). This can be due to an effect of temperature, since the temperature range analyzed for sPS was higher than that adopted for aPS, or to differences in free volumes between the two materials. Due to the narrow range accessible to the technique adopted, neither a clear effect of the temperature nor of the shear rates can be evinced from the data which do not allow any deeper analysis.

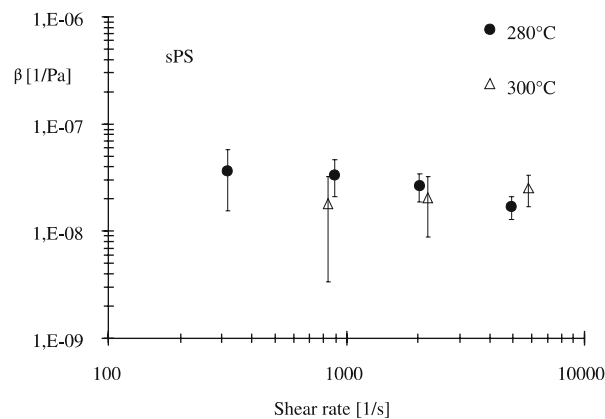


Figure 4. Values of the parameter β for sPS obtained analyzing the data of Figure 2 by means of eq. (11).

In Figure 5, the values of β for aPS obtained by applying the classical analysis to the Bagley plots (namely by adopting eq. (7)) are compared with the results obtained in this work for aPS and already reported in Figure 3. As expected, the values found by adopting the classical analysis of non-linear Bagley plots are higher (by factor 2) than the results obtained by means of the eq. (11). The same observation also holds for sPS. A comparison of the results obtained by the two analysis of non linearities provides an estimation of the error performed by adopting a series expansion.

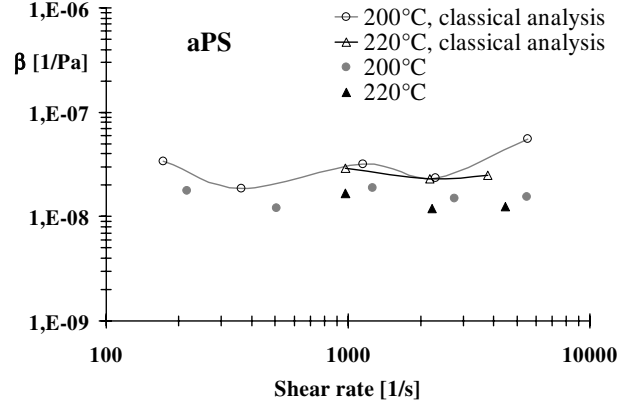


Figure 5. Comparison between the results obtained analyzing the data of Figure 1 (a and b) by means of eq. (7) (classical analysis) and of eq. (11) (already reported in Figure 3).

Cross-Vogel analysis of data

As mentioned above, the values of shear stress at room pressure, σ_{ow} , obtained by data regression are quite reliable. The viscosities at room pressure for both materials could thus be easily obtained by the data reported in Figures 1 and 2. The experimental values are reported in figure 6 and 7 for aPS and sPS, respectively. It is worth mentioning that these data are in good agreement with other rheological characterizations found in the literature for both materials [12, 13].

The following Cross-Vogel model was adopted to describe the data of viscosity

$$\eta = \frac{\eta_N}{1 + \left(\frac{\eta_N \gamma'}{\tau^*}\right)^{1-n}} \quad (14)$$

$$\eta_N = \eta^* \exp\left(\frac{A + kP}{T - T_{ref}}\right) \quad (15)$$

where γ' is the shear rate. The parameters which allowed the best description of data are reported in Table 1 (the parameter k was obviously set to zero in the regression of the parameters of equations (14) and (15)). Model predictions are compared with experimental data in figures 6 and 7.

The parameter β describing the effect of pressure on viscosity according to the Barus equation (eq. (2)) is easily obtained from equations (14) and (15) as follows

$$\beta = \frac{1}{\eta} \frac{\partial \eta}{\partial \eta_N} \frac{\partial \eta_N}{\partial P} = \frac{1 + n \left(\frac{\eta_N \gamma'}{\tau^*}\right)^{1-n}}{1 + \left(\frac{\eta_N \gamma'}{\tau^*}\right)^{1-n}} \frac{k}{T - T_{ref}} \quad (16)$$

Only the value of k in eq. (16) remains to be defined, and this can be done on the basis of all data reported in Figure 3 (for aPS) and in Figure 4 (for sPS). Of course, the choice of the best value for k was done by giving a larger weight to the data having the smallest uncertainty. The values found, which give rise to the comparison reported in Figures 8 and 9 are $k=1.18 \cdot 10^{-5} \text{ }^\circ\text{C/Pa}$ for aPS and $k=1.75 \cdot 10^{-5} \text{ }^\circ\text{C/Pa}$ for sPS.

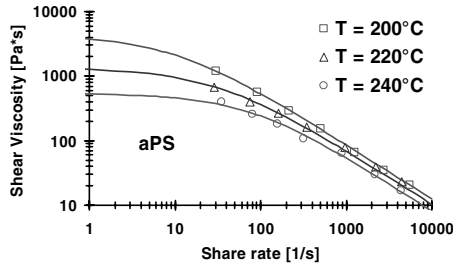


Figure 6. Shear viscosity as function of shear rate for aPS. Symbols: experimental data; Solid line: model predictions (eq. 14-15).

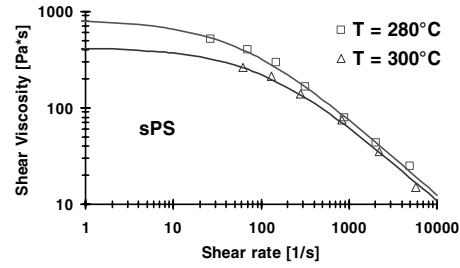


Figure 7. Shear viscosity as function of shear rate for sPS. Symbols: experimental data; Solid line: model predictions (eq. 14-15).

Table 1. Values of the parameter found by a best fitting analysis of viscosity data on the basis of equations (14) and (15).

	aPS	sPS
η^* [Pa s]	0.63	0.73
A [°C]	1152	1358
T_{ref} [°C]	69.5	86.5
n [-]	0.16	0.19
τ^* [Pa]	41651	47739

According to Equation (16), β is a function of temperature, pressure and shear rate, and the effect of each of these variables is clear from the plots reported in Figures 8 and 9. It can be noticed, however, that in the range analyzed in this work the effects of these variables are rather weak and justify the experimental observation of a substantial independence of β upon shear rate and temperature. The effect of pressure is rather relevant only at shear rates lower than about 100/s, where however the lowest pressure levels are encountered.

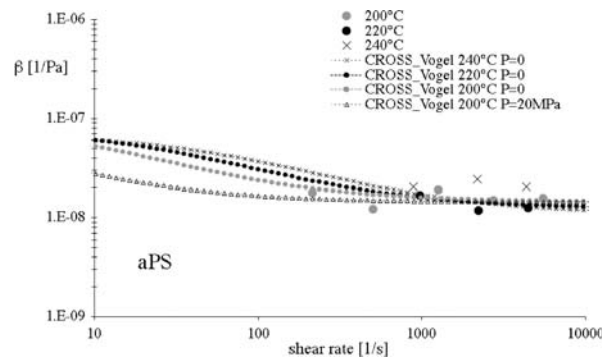


Figure 8. Comparison between the experimental data and results of eq. (16) for aPS.

Effect of dissipative heating and melt compressibility

When β is calculated from non-linear Bagley plots it is necessary to keep into account viscous heating which also induces a curvature in pressure profiles. The simplest method to account for the effect of dissipative heating is to assume adiabatic flow,

which allows to obtain a linear relationship between the temperature rise and the pressure drop [15] once it is assumed that the product between density and specific heat is a constant:

$$\rho C_p (T - T_i) = -(P_i - P) \quad (17)$$

Considering that the viscosity dependence on temperature and pressure jumps can, at a first approximation, written as

$$\eta = \eta_0 e^{\beta_{\text{corr}} P - \alpha(T - T_0)} \quad (18)$$

where the subscript “corr” means that the effect of dissipative heating is kept into account. The substitution of equations (17) and (18) into eq. (1) leads to

$$\sigma_{\text{ow}} 4 \frac{L}{D} = \frac{e^{-\frac{\alpha}{\rho C_p} P_0} - e^{-\beta_{\text{corr}} P_0}}{\frac{\alpha}{\rho C_p} - \beta_{\text{corr}}} \quad (19)$$

which, with respect to Equation (3), also keeps into account the effect of dissipative heating. Operating series expansion of the exponential terms in Equation (19), and following the reasoning presented in the section “*Alternative approach*”, one can obtain the following equation

$$\frac{L}{D} = -\frac{1}{4\sigma_{\text{ow}}} \frac{\left(\beta_{\text{corr}} - \frac{\alpha}{\rho C_p}\right)}{2} P_p^2 + \frac{1}{4\sigma_{\text{ow}}} P_p - \frac{e}{D} \quad (20)$$

According to this equation, the capillary aspect ratio is still expressed as a function of the experimentally determined pressure P_p in a quadratic form, but it is clear that the effect of dissipative heating introduces an upward curvature which counteracts the effect of pressure on viscosity [11]. This means that, if dissipative heating is kept into account, the values of β will be higher.

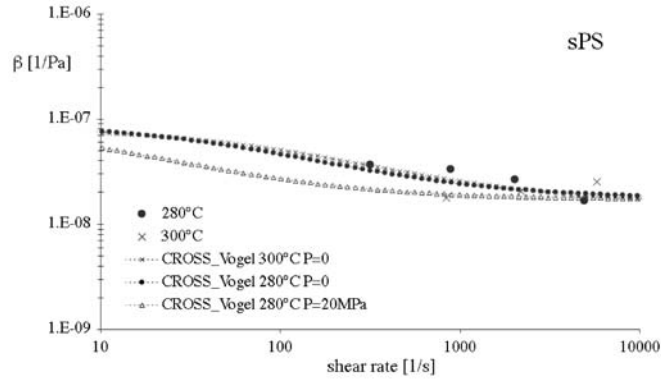


Figure 9. Comparison between the experimental data and results of eq. (16) for sPS.

The parameter α describing the effect of temperature on viscosity according to Equation (18) is easily obtained from equations (14) and (15) as follows

$$\alpha = \frac{1}{\eta} \frac{\partial \eta}{\partial \eta_N} \frac{\partial \eta_N}{\partial T} = \frac{1 + n \left(\frac{\eta_N \dot{\gamma}}{\tau^*} \right)^{1-n}}{1 + \left(\frac{\eta_N \dot{\gamma}}{\tau^*} \right)^{1-n}} \frac{A + kP}{(T - T_{\text{ref}})^2} \quad (21)$$

and thus the error made neglecting the effect of dissipative heating is readily calculated as

$$\frac{(\beta_{\text{corr}} - \beta)}{\beta} = \frac{\alpha}{\beta} \frac{1}{\rho C_p} = \frac{1}{\rho C_p} \frac{A + kP}{T - T_{\text{ref}}} \quad (22)$$

Since for both materials considered in this work the density of the melt is within 910-1000 Kg/m³ (for pressures up to 100MPa) [13] and C_p is about 2000J/KgK [13], the values of β_{corr} for both materials can be estimated to be about 20-25% higher than the values of β reported above. This means that also the values found for k in Equation (15) should be about 20-25% higher than those reported above. It has to be mentioned that these percentages fall well within the uncertainties of the experimental data.

As far as the effect of melt compressibility is concerned, being α and β for both materials about a factor 100 higher than the thermal expansion and compressibility coefficients, respectively, it can be concluded [16] that it is negligible.

Comparison with the literature

The estimation of the effect of pressure on viscosity for aPS has been performed in the past by several authors and by different methods. A comparison of literature results [1-4, 8, 10, 14] regarding the parameter β is reported in Figure 10, together with the values found in this work (only the temperature of 200°C is reported). As clear from the figure, literature values are quite scattered, and only some of the authors take into account the dependence on shear rate. The values found in this work fall in the range of literature data (which however cover a very wide area). With respect to the most recent literature results obtained by high pressure capillary rheometers (namely by Kadijk and Van Den Brule [1], Couch and Binding [3] and Sedlacek et al. [4]) the values found in this work seem to be only slightly larger. Obviously the technique adopted in this work is not sensible enough to reach the low shear rate region, but it allowed to easily estimate the effect of pressure on viscosity in a range of shear rates of interest for polymer processing.

Conclusions

In this work, the effect of pressure on the viscosity of two polystyrene melts, an atactic and a syndiotactic one, was estimated by means of the analysis of non-linearities in Bagley plots. Data clearly show that for both materials the average value of β is in the range 1-3 10⁻⁸Pa⁻¹. No relevant effect of temperature and shear rate could be detected in the range of variables analyzed.

The values of β found for sPS are slightly higher than those collected on aPS. This could be due to an effect of temperature or to differences in free volumes between the two materials. The technique, however, is not sensitive enough to obtain conclusions regarding effects of molecular structure or free volume, so a further analysis is needed.

The data obtained were described by means of a Cross-Vogel model, which reproduces the main features of experimental data. In particular, for both materials, the model describes, in the ranges of shear rates analyzed in this work, a substantial independence of β on temperature, pressure and shear rates.

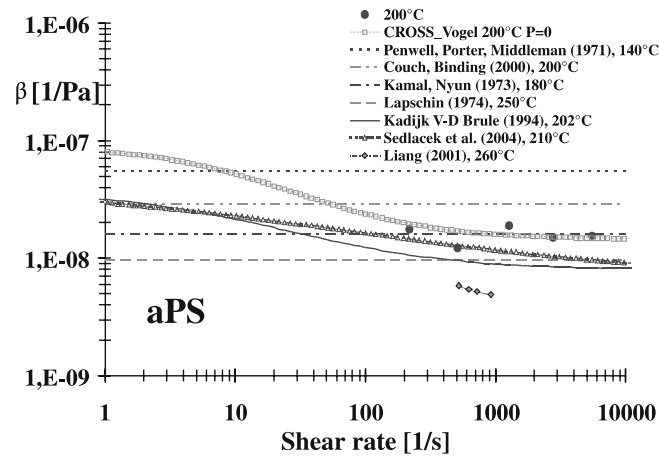


Figure 10. Comparison between literature results on the effect of pressure on viscosity for aPS and some of the results obtained in this work.

A comparison with the literature was presented for atactic polystyrene. With respect to literature results, the data found in this work are of the correct order of magnitude, and only slightly higher than the most reliable values found by high pressure capillary rheometers.

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