NOVEL ASPECTS OF THE RHEOLOGY OF SYNDIOTACTIC POLYPROPYLENE: PRESSURE DEPENDENCE OF VISCOSITY

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ABSTRACT

Experimental results of the pressure-viscosity relationship of metallocene catalyzed isotactic (miPP) and syndiotactic polypropylene (sPP) are presented and compared with theoretical results obtained from a thermodynamical approach. It is observed that sPP offers slightly lower values of $b = \frac{\partial \ln \eta}{\partial P}$ than miPP.

INTRODUCTION

Although data of the pressure coefficient of viscosity, $b = \frac{d \ln \eta}{dP}$, of conventional polypropylenes are available in the literature[1], pressure effects have not been investigated yet for metallocene catalysed isotactic (miPP) and syndiotactic polypropylenes (sPP). It is known that the almost perfect stereoregularity of sPP leads to a particular rheological response, characterized by larger values of the relaxation time, the Newtonian viscosity and the entanglement modulus G_N^0, than isotactic polypropylene[2]. Conformational parameters, like the characteristic ratio, which are responsible of these peculiarities, account also for the higher activation energy of flow, Ea, found in sPP. Our thermodynamic analysis of the pressure dependence of viscosity, implies a correlation of b with Ea, as well as with the compressibility coefficient, β.

In this communication, experimental results of the pressure-viscosity relationship of isotactic and syndiotactic polypropylenes are presented. Pressure-volume-temperature (PVT) experiments are also carried out to determine β. The analysis of the results allows offering novel aspects of the rheology of metallocene catalysed syndiotactic polypropylenes.

EXPERIMENTAL

The molecular characteristics of the investigated isotactic and syndiotactic polypropylenes are presented in Table 1.

Table1. Structural parameters for isotactic and syndiotactic polypropylenes.

Material	tacticity	Mw	Mw/Mn
miPP	mmmm 92.6%	224300	4.2
sPP	rrrr 77%	1481300	3.95

A Göttfert 2000 extrusion rheometer equipped with a set of transducers to monitor the pressure profile during the flow in a slit die (L=100mm, h=10mm, w=0.5mm), has been used to analyze the effect of shear rate, temperature, and pressure on viscosity. In particular the pressure coefficient $b = \frac{d \ln \eta}{dP}$ is determined using a parabolic fit of the pressure vs flow coordinate Z:

$$P = d + eZ + fZ^2 \qquad (1)$$

This allows obtaining b as:

$$b = \frac{2f}{e^2} \qquad (2)$$

The compressibility coefficient,

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

has been obtained using a PVT measuring apparatus Haake PVT 100.

RESULTS AND DISCUSSION

The values of the pressure coefficient of viscosity obtained using equation 2 are displayed in Fig 1, as a function of the shear rate.

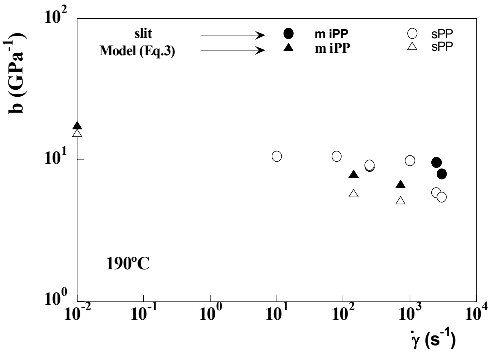

Figure 1. Pressure coefficient of viscosity,b, as a function of shear rate for isotactic, iPP, and syndiotactic polypropylene, sPP

Both, isotactic and syndiotactic polypropylene show a decreasing tendency of b with shear rate similar to that observed for other polymers.[3] Although there is a certain scatter, it can be stated that sPP offers slightly lower values of b. We have to point out that the data have been obtained using an experimental method (flow in a slit) which, under certain conditions, can lead to non negligible errors[4]. A comparative study of the use of different experimental methods to determine b is currently in progress [5].

Assuming the thermodynamic analysis of the effect of pressure on viscosity proposed by Goldblatt and Porter[6], and considering an Arrhenius-like temperature dependence of viscosity, the following equation can be obtained:

$$b = \frac{E_a}{RT}\frac{(\beta V)_T}{(\beta V)_{T_g}}\frac{dT_g}{dP} \qquad (3)$$

The parameters involved in this equation are presented in Table 2 and the corresponding b values are displayed in Fig. 1, together with experimental data. We remark that in the equation 3 the effect of shear rate on b is only due to the variation of Ea with $\dot{\gamma}_{21}$, wich is determined in the extrusion rheometer. The results obtained from the thermodynamic model (Eq. 3) confirm that sPP is less susceptible to pressure effect than iPP.

Table 2. Parameter used in Equation 3. obtained b, extrusion flow and PVT measurements.

	iPP			sPP		
$\frac{(\beta \mathrm{v})_T}{(\beta \mathrm{v})_{Tg}}$	$\frac{7.82910^{-10}}{2.07410^{-10}}$			$\frac{7.69810^{-10}}{2.7410^{-10}}$		
dTg/dP (º/bar)	0.02			0.02		
$\dot{\gamma}_{21}$ (s^{-1})	newtonian	144	722	newtonian	144	722
Ea (Kcal/mol)	9.7	4.66	3.9	11.8	4.41	3.95
b (GPa^{-1})	17.6	8	6.8	15.6	5.8	5.2

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Evaluation of pressure dependence of viscosity for some polymers using capillary rheometer

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ABSTRACT

The pressure dependence of viscosity of commercial polymers was studied using the modified capillary rheometer. The polymers under investigation were low-density polyethylene (LDPE), polystyrene (PS) and poly (oxymethylene) (POM). For each material, the pressure dependent viscosity was determined at different shear rates up to a pressure of 100 MPa.

INTRODUCTION

The influence of pressure on the polymer melt viscosity is often largely overlooked. The assumption of pressure-independent viscosity can be justified for most extrusion operations, whereas in the case of injection moulding this assumption is much more questionable. Especially in thin-wall injection moulding applications pressures in excess of 100 MPa frequently occur, which can cause a significant increase in the polymer viscosity. For example, when simulating the injection moulding process the neglect of these pressure-dependent effects may lead to largely inaccurate predictions of pressure.

Previous studies on the pressure dependence of viscosity of polymer melts have recently been reviewed in detail by Binding et al. [1] and Goubert et al. [2]. Even though the first study on this topic appeared in the late 1950s, the available body of experimental data in the open literature is still quite limited. The obvious reason for this is the fact that it is difficult to directly measure the dependence of viscosity on pressure. The advantages and disadvantages of existing methods have been evaluated by Goubert et al. [2]. They concluded that a simple, yet reasonably accurate, way of conducting viscosity measurements at elevated pressures is to use the capillary rheometer, which is modified by attaching an additional chamber with an adjustable constriction below the capillary die. This type of technique was pioneered by Driscoll and Bogue [3], and subsequently employed by several other researchers (e.g., [1, 2, 4, 5]).

In this study, such a modified capillary rheometer is used to evaluate the effect of pressure on the viscosity of low-density polyethylene (LDPE), polystyrene (PS) and poly (oxymethylene) (POM). It is known from earlier studies (e.g., [2]) that the viscosity of PS has a considerably stronger dependence on pressure than that of LDPE, whereas the pressure dependence of viscosity of POM is not well known at present. POM is a polymer that is increasingly widely used particularly for injection moulding applications and therefore it is of practical interest to examine how its viscosity depends on the pressure in relation to LDPE and PS.

EXPERIMENTAL

Materials

The materials studied with regard to the pressure dependence of viscosity are low-density polyethylene (LDPE), polystyrene (PS) and poly (oxymethylene) (POM). LDPE grade (Lupolen 1840H, Basell) used is a long chain branched semi-crystalline homopolymer. PS (Polystyrol 143E, BASF) is an amorphous, crystal clear polymer with benzene ring as a pendant group in the molecule chain. POM (Hostaform C 9021, Ticona) is a linear semi-crystalline copolymer having an oxygen atom in the base body. Molecular structure of each monomer can be seen in Fig. 1.

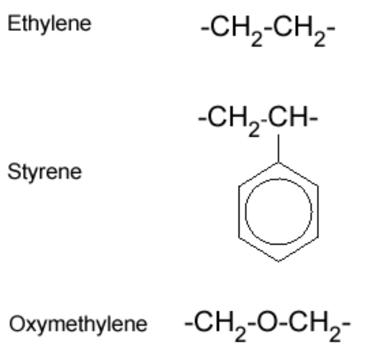

Figure 1. Molecular structure of ethylene, styrene and oxymethylene monomer respectively.

Apparatus and measurements

The experiments were conducted using the capillary rheometer Göttfert Rheograph 6000. The standard equipment was modified by an additional unit called the counter pressure chamber (CPC), also manufactured by Göttfert. The CPC surrounded by a heating element is mounted below the rheometer barrel and capillary die. The pressure level in the chamber can be adjusted with a conical valve bolt mounted inside the CPC body. Construction of the CPC is presented in Fig 2.

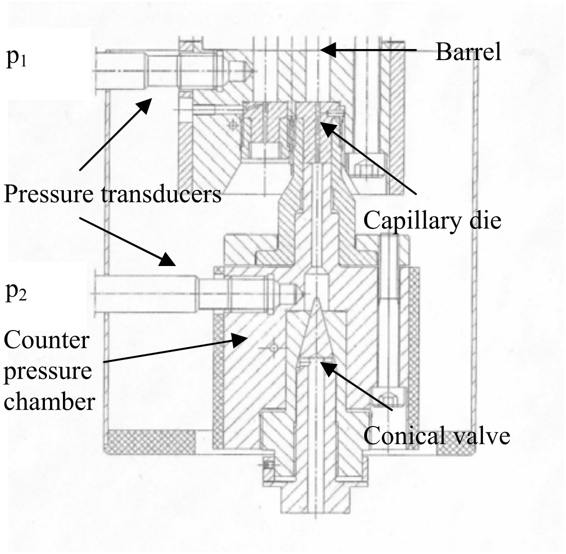

Figure 2. Schematic drawing of counter pressure chamber [6].

During the measurements, the pressure was monitored at two locations by pressure transducers: in the barrel just above the capillary and in the pressure chamber right below the capillary. The test procedure was initiated by selecting a constant piston speed, which corresponds to a constant apparent shear rate at the capillary wall. At the beginning of the test, the position of the conical valve was 180° open. At this point, the pressure in the chamber was close to atmospheric. Once the pressures had stabilized, i.e., the flow had reached a steady state, both transducer readings were recorded simultaneously. The constriction was then tightened by turning the valve, which resulted in the increase of both the barrel and chamber pressures. When stable pressures were again established and recorded, a further constriction was made and this procedure was continued until the barrel became empty or the maximum capacity of either pressure transducer was reached. The recommended maximum operating (mean) pressure for the device is 120 MPa.

Each of the polymer was tested at a temperature of 200ºC and at apparent shear rates of 50, 200 and 500 1/s. Two capillaries were used having a diameter of 1 mm and length-to-diameter ratios (*L*/*D*) of 10 and 20. Pressure transducers with maximum capacities of 140 and 100 MPa were employed for upstream and downstream pressure recordings, respectively.

Estimation of viscosity

The pressure drop across the capillary (Δp) and the mean pressure in the capillary (p_m) are defined as follows:

$$\Delta p = p_1 - p_2 \tag{1}$$

$$p_m = (p_1 + p_2)/2 \tag{2}$$

Here, p_1 and p_2 are the pressures recorded before and after the capillary, respectively. As was mentioned above, the measurements were made with two different capillaries in order to allow the Bagley correction to be performed. The pressure drops associated with the capillaries of L/D = 10 and 20 are denoted as $(\Delta p)_{10}$ and $(\Delta p)_{20}$, respectively. Assuming a linear extrapolation to zero capillary length, the entrance pressure drop, Δp_E. takes the form

$$\Delta p_E = 2(\Delta p)_{10} - (\Delta p)_{20} \tag{3}$$

The Bagley corrected viscosity for a given apparent wall shear rate, $\dot{\gamma}_a$ (= $32Q/\pi D^3$), can now be written as

$$\eta_a = \frac{\Delta p - \Delta p_E}{4(L/D)\,\dot{\gamma}_a} \tag{4}$$

Note that Δp in this equation is $(\Delta p)_{10}$ or $(\Delta p)_{20}$ depending on whether the L/D value of 10 or 20 is used (both yield the same result). Because only three apparent shear rates were considered here, the Rabinowitsch correction was not applied to the measured data.

RESULTS AND DISCUSSION

At each apparent shear rate (50, 200 and 500 1/s), the raw data obtained from the measurements contains the values of $(\Delta p)_{10}$ and $(\Delta p)_{20}$ at different values of p_m. Each experiment was performed twice in order to check the repeatability of the results. The data points obtained, including both test series, are given in Figs. 3-5 for LDPE, PS and POM, respectively. It can be observed that the scatter in the experimental data is relatively small.

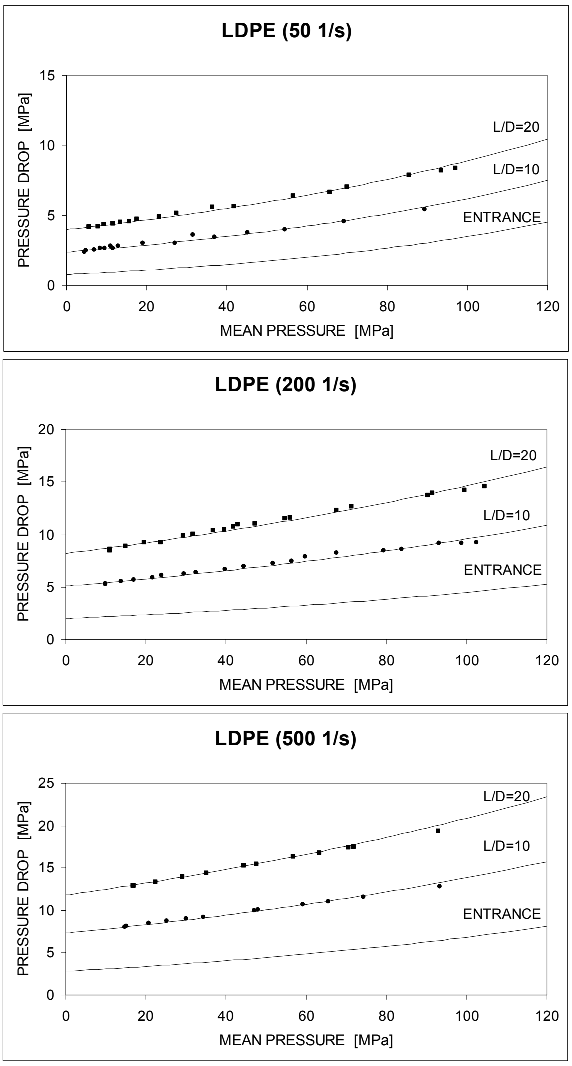

Figure 3. Pressure drop vs. mean pressure for LDPE at shear rates of 50 200 and 500 1/s.

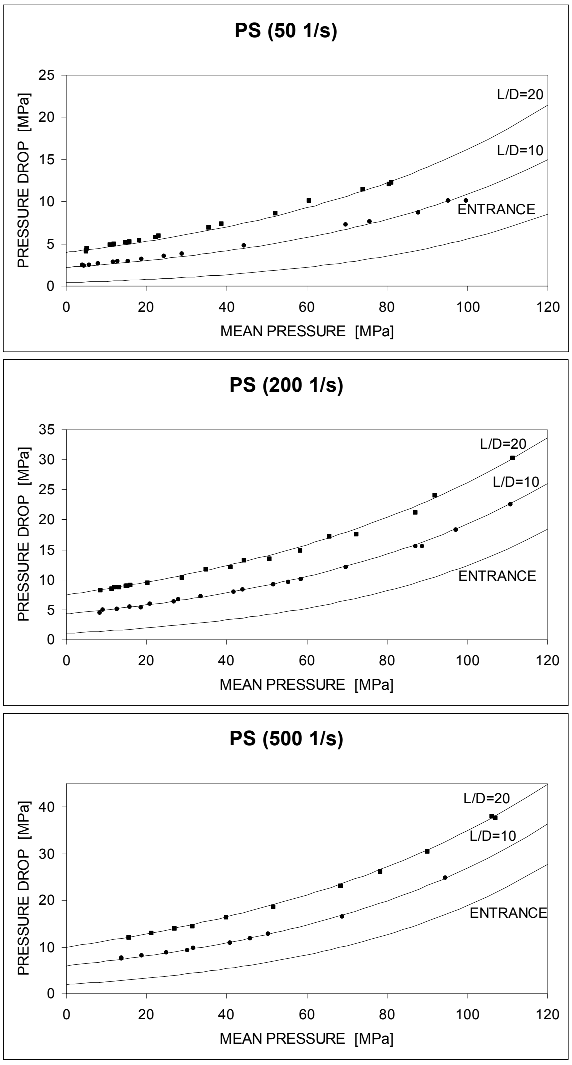

Figure 4. Pressure drop vs. mean pressure for PS at shear rates of 50 200 and 500 1/s.

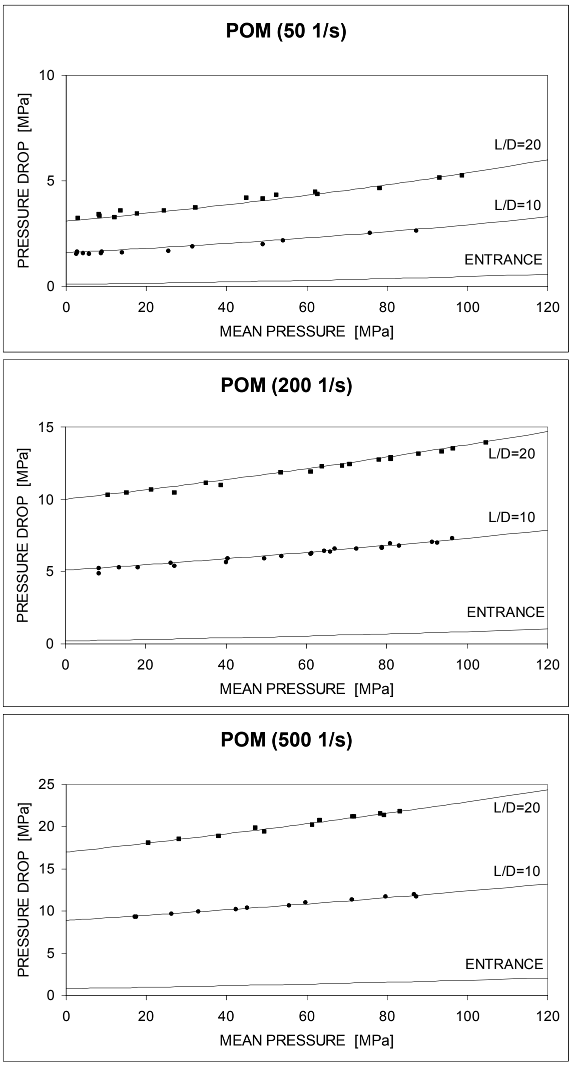

Figure 5. Pressure drop vs. mean pressure for POM at shear rates of 50 200 and 500 1/s.

The analysis of the experimental data would be most straightforward if the tests for all capillaries and apparent shear rates would have been performed at the same mean pressure levels. In principle, this could be achieved by suitable valve adjustments. Owing to the fact that the mean pressure within the capillary cannot be controlled directly this would, however, be a very time-consuming procedure and was not accomplished here. Instead, to facilitate the analysis, the experimental raw data points were fitted to exponential functions, as indicated in Figs. 3-5.

Using the fitted functions for $(\Delta p)_{10}$ and $(\Delta p)_{20}$, the Bagley corrections were first applied to the data according to Eq. (3) in order to determine the entrance pressure drops; the resulting curves for Δp_E as a function of p_m are depicted in Figs. 3-5. It can be noticed that for PS the entrance pressure drop is strongly dependent on the mean pressure and at high pressures it represents even 50% of the uncorrected pressure drop with the capillary of $L/D = 20$ (and of course more with $L/D = 10$). The entrance pressure drop effects appear to be fairly significant with LDPE too, whereas with POM they play a minor role.

Now, Eq. (4) can be used to calculate η_a as a function of p_m for each apparent shear rate; the results attained are given in Fig. 6. This figure reveals that the increase of viscosity with pressure is more pronounced for PS than for LDPE, as expected on the basis of previous studies. Among the polymers tested, the viscosity of POM seems to be least sensitive to pressure.

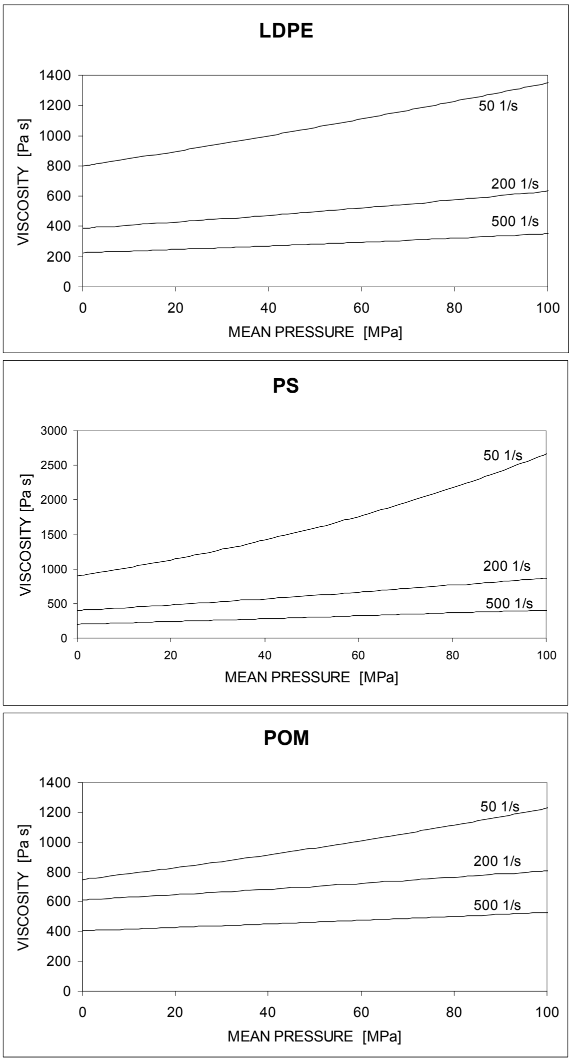

Figure 6. Viscosity vs. mean pressure at different shear rates for LDPE PS and POM respectively

For modelling purposes, the dependence of viscosity on temperature and pressure is usually accounted for by appropriate shift factors. For the pressure shift factor, an exponential function is commonly used, that is

$$a_p = \exp[\beta(p - p_0)] \tag{5}$$

where β is a material-dependent pressure coefficient.

Based on the present viscosity measurements, the pressure coefficient values were determined for each polymer. The values obtained with different apparent shear rates are listed in Table 1.

Table 1. Pressure coefficients

Material	$\dot{\gamma}_a$ [1/s]	β [1/MPa]
PS	50	0.0109
	200	0.0078
	500	0.0072
LDPE	50	0.0052
	200	0.0049
	500	0.0045
POM	50	0.0049
	200	0.0028
	500	0.0027

CONCLUSIONS

The modified capillary rheometer has been used to investigate the pressure dependence of viscosity of low-density polyethylene (LDPE), polystyrene (PS) and poly (oxymethylene) (POM) with pressures up to 100 MPa. In accordance with earlier studies, it was found that the influence of pressure on the melt viscosity is appreciably stronger for PS than for LDPE. In the case of POM, the pressure-dependent effects turned out to be of minor importance compared to both PS and LDPE.

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