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.

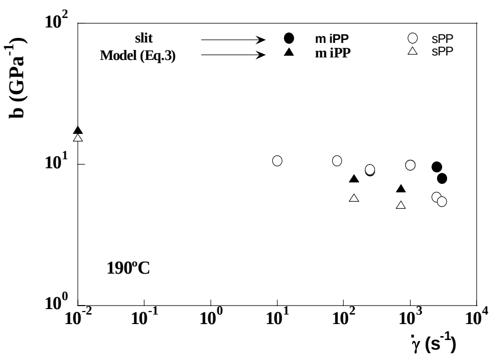

Figure 1. Pressure coefficient of viscosity,b, as a function of shear rate for isotactic, iPP, and syndiotactic polypropylene, sPP

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		
$\frac{(\beta V)_T}{(\beta V)_{Tg}}$	$\frac{7.82910^{-10}}{2.07410^{-10}}$			$\frac{7.69810^{-10}}{2.7410^{-10}}$		
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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